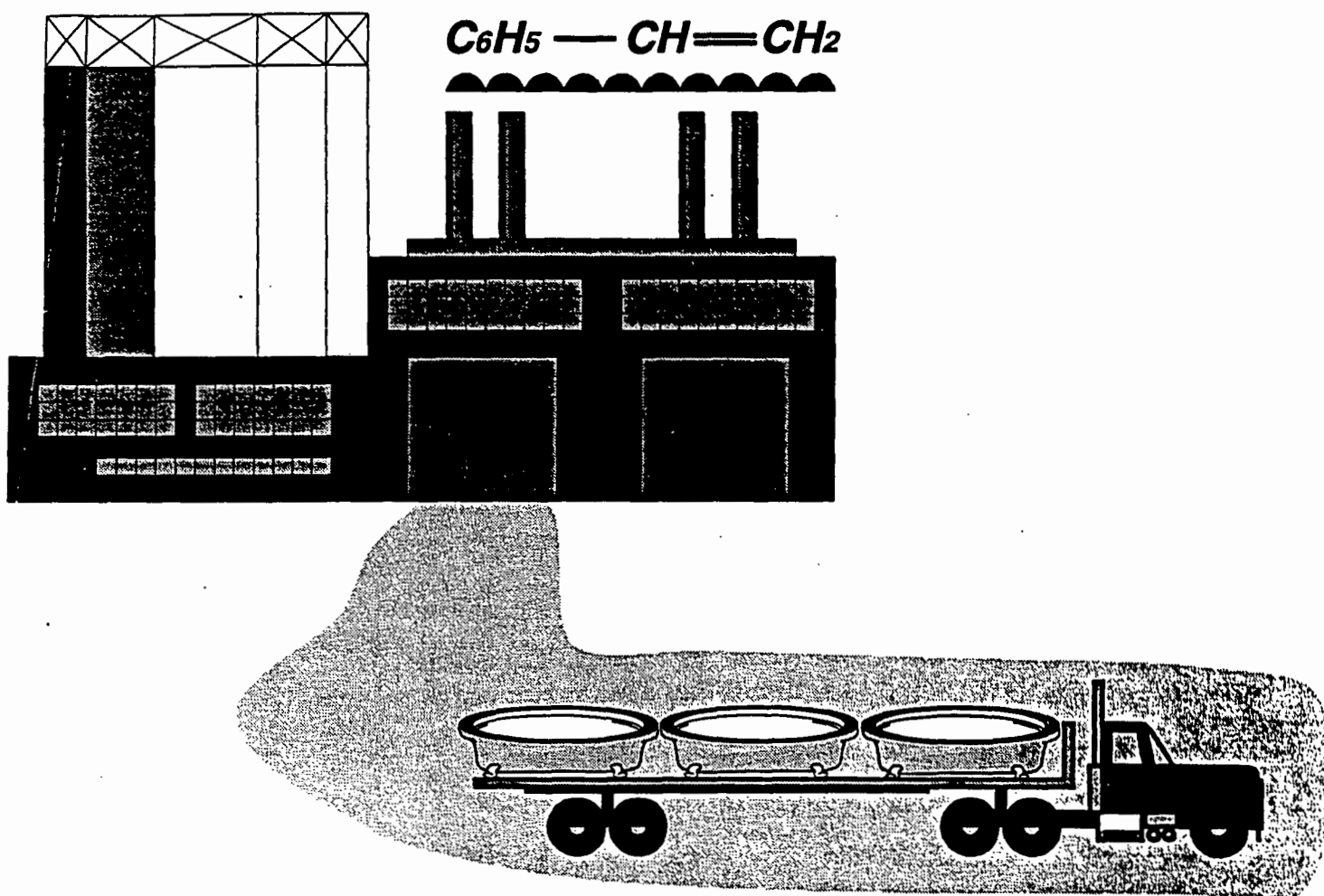


EPA Evaluation of Styrene Emissions From a Shower Stall/Bathtub Manufacturing Facility



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Prepared for Office of Air Quality Planning and Standards

Prepared by Air and Energy Engineering Research Laboratory

FOREWORD

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**EVALUATION OF STYRENE EMISSIONS FROM A
SHOWER STALL/BATHTUB MANUFACTURING FACILITY**

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ABSTRACT

Current EPA emission factors (AP-42) for styrene emissions from the production of polyester resin reinforced plastic products represent a composite of spraying and post-spraying emissions from shower stall/bathtub manufacturing plants that use compressed air-powered spray guns to apply catalyzed styrene resins to prepared molds. Because each step of manufacture (gel coating, first-stage spray lay-up, and second-stage spray lay-up) creates large surface areas from which volatile styrene monomer can evaporate, non-spraying emissions can constitute a large fraction of the styrene emitted to the atmosphere. Thus, it is of interest to quantify the level of non-spraying styrene emissions characteristic of this industry.

In this study, emissions measurements were carried out at a representative facility (Eljer Plumbingware in Wilson, NC) that manufactures polyester resin reinforced shower stalls and bathtubs by spraying styrene-based resins onto molds in vented, open, spray booths. Styrene emissions were characterized for the three stages of manufacture by measuring styrene concentrations at the vents of spray booths used in each part of the process. In addition, styrene concentrations were measured at each ventilation fan exhaust. Emission levels were determined using EPA Method 18 to obtain integrated emissions samples and total hydrocarbon (THC) analyzers to measure continuous emissions levels during the EPA Method 18 sampling.

Analysis of the EPA Reference Method data indicates that: (1) styrene monomer is the only volatile organic compound released in this process; (2) overall, approximately 4% of all material sprayed is lost to atmospheric emissions as styrene (approximately 19% of all styrene sprayed); and (3) emissions vary for each phase of manufacture, with post-spraying emissions of styrene (from curing molds) constituting a large part, approximately 29% of all emissions.

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Metric to Nonmetric Conversions

Readers more familiar with nonmetric units may use the following factors to convert to that system.

<u>Metric</u>	<u>Multiplier</u>	<u>Yields Nonmetric</u>
kPa	1450.38	psig
kPa	4.0145	in. H ₂ O
°C	1.8T + 32	°F
l (1000 cm ³)	0.26417	gal.
m	3.2808	ft
m ²	10.7637	ft ²
m ³	35.3134	ft ³
kg	2.2026	lb
1000 kg (metric ton)	1.1023	ton (short)

SECTION 1

INTRODUCTION

Current EPA emission factors (Table 1) for styrene emissions from the production of polyester resin reinforced plastic products represent a composite of spraying and post-spraying emissions (from curing molds) from shower stall/bathtub manufacturing plants that use compressed air-powered spray guns to apply catalyzed styrene resins to prepared molds.¹ Because each step of manufacture creates large surface areas from which volatile styrene monomer can evaporate, post-spraying emissions can constitute a large fraction of the styrene emitted to the atmosphere. Thus, it is of interest to quantify the level of spraying and post-spraying styrene emissions characteristic of this industry.

Shower stalls and bathtubs are among the many kinds of products fabricated from liquid polyester resin that has been extended with various inorganic filler materials and reinforced with glass fibers. These composite materials are often referred to collectively as fiberglass reinforced plastic (FRP) or "fiberglass". Depending on the size, shape, and intended use, any one of several manufacturing processes can be used for fabrication. For the manufacture of shower stalls and bathtubs, the preferred technique is spray lay-up or sprayup. Regardless, all of these processes involve the application of a liquid resin that is mixed with a catalyst to initiate polymerization. In polymerization, a liquid unsaturated polyester is cross-linked with a vinyl-type monomer, usually styrene, by the action of the catalyst. Common catalysts are organic peroxides, typically methyl ethyl ketone peroxide (MEKP) or benzoyl peroxide. Resins may contain inhibitors, to avoid self-curing during resin storage, and promoters, to allow polymerization to occur at lower temperatures.^{2,3}

In the production of fiberglass shower stalls and bathtubs, exhaust air from the spray booths used for mold-coating and plant ventilation air outlets represent the major point sources of VOC emissions. Thus, at a particular facility, the number of manufacturing steps that involve the spraying of styrene-based resins, the amount of styrene sprayed in each step of manufacture, and the amount of

Table 1. Emission Factors for Uncontrolled Polyester Resin^{1,4}

PRODUCT FABRICATION PROCESSES (a) (100 x mass of VOC emitted/mass of monomer input)						
Process	Resin		Emission Factor Rating*	Gel Coat		Emission Factor Rating*
	NVS	VS(b)		NVS	VS(b)	
Hand lay-up	5 - 10	2 - 7	C	26 - 35	8 - 25	D
Spray lay-up	9 - 13	3 - 9	B	26 - 35	8 - 25	B
Continuous lamination	4 - 7	1 - 5	B	(c)	(c)	
Pultrusion(d)	4 - 7	1 - 5	D	(c)	(c)	
Filament winding(e)	5 - 10	2 - 7	D	(c)	(c)	
Marble casting	1 - 3	1 - 2	B	(f)	(f)	
Closed molding(g)	1 - 3	1 - 2	D	(c)	(c)	

(a) Ranges represent the variability of processes and sensitivity of emissions to process parameters. Single value factors should be selected with caution. NVS = nonvapor-suppressed resin. VS = vapor-suppressed resin.

(b) Factors are 30-70% of those for nonvapor-suppressed resins.

(c) Gel coat is not normally used in this process.

(d) Resin factors for the continuous lamination process are assumed to apply.

(e) Resin factors for the hand lay-up process are assumed to apply.

(f) Factors unavailable. However, when cast parts are subsequently sprayed with gel coat, hand and spray lay-up gel coat factors are assumed to apply.

(g) Resin factors for marble casting, a semiclosed process, are assumed to apply.

* Emission factors developed from the results of facility source tests (B Rating), laboratory tests (C Rating), and through technology transfer estimations (D Rating).²

styrene that is volatilized during the spraying and curing of molds determines the amount of styrene emitted to the atmosphere.

This study was undertaken to quantify styrene emission factors at a shower stall/bathtub manufacturing plant determined by the EPA to be a representative facility. Once styrene emissions were measured, the emissions measurements and raw material usage data from the plant were used to determine emission factors for each phase in the manufacturing process.

Testing was carried out at Eljer Plumbingware, in Wilson, North Carolina and was part of a larger effort that also involved the evaluation of a pilot-scale liquid chemical scrubber for styrene removal. Styrene emissions measurements were originally scheduled for the week of June 14, 1993 and the liquid chemical scrubber evaluation was originally scheduled for the following week. Because the plant was operating on a four-day production week during this time (Monday through Thursday), instead of the five-day production week that had been expected, emissions testing had to be extended through Monday, June 21, 1993 to obtain a suitable set of emissions data. A full day of testing could not be carried out on Monday because portions of that day had to be devoted to preparing for the upcoming liquid chemical scrubber evaluation.

Section 2 contains a detailed description of the facility and sampling locations. Detailed descriptions of the sampling methodology are presented in Section 3 and the results of this evaluation along with a discussion of these results are presented in Section 4. The quality assurance and quality control measures taken during this evaluation as well as the results of these measures are contained in the Quality Control Evaluation Report in Appendix A.

SECTION 2

PROJECT DESCRIPTION

EXPERIMENTAL APPROACH

Styrene is an integral part of the industrial process that produces fiberglass bath tubs and shower stalls. In the first step of this manufacturing process, styrene monomer is mixed with polyester resin and a pigment to create a "gel coat" that is sprayed onto a previously prepared mold. Methyl ethyl ketone peroxide (MEKP) catalyst is added to the mix externally as it exits the compressed air-powered spray gun used to apply the mix to a mold. Molds are reusable and before each use the mold is waxed and coated with a mold-release agent that also helps to provide a high gloss to the finished product. In subsequent manufacturing steps, styrene and polyester resin are mixed with inert fillers and sprayed onto the previously coated mold along with chopped fiberglass. Between each application the fiberglass strands are compacted on the mold by manual rolling after which the coated mold is set aside while the resin is allowed to cure. Because curing is an exothermic process, succeeding manufacturing steps are usually not carried out until the coated mold has cooled. Fiberglass provides structural support for the finished article, while the cross-linked styrene and polyester resin act as a glue to hold the matrix together, and the inert fillers provide additional structural support and can also provide fire retardant properties. The final stage of manufacture is to separate the finished fiberglass product from the mold, and prepare it for shipment.

The purpose of this project is to develop quantitative emission factors specific to a spray layup polyester resin shower stall and bathtub manufacturing process. To develop these emission factors, styrene emissions were quantified from every point of air exhaust to the atmosphere at a fiberglass shower stall and bathtub manufacturing plant located in Wilson, North Carolina. Specifically, the following information was required to develop quantitative emission factors for styrene:

- Determination of the emission rate of styrene emitted from process exhaust vents during normal production.

- Determination of the emission rates of any fugitive styrene emissions during storage, transfer or mixing of the resin or gel coat by process material balance.
- Relation of emission rates of styrene to the amount of raw materials used and to the number of units produced by collecting process data during tests of process exhaust vents, measuring the time required to complete each unit, determining material balances for the production process, and by computing emission factors for vents and for fugitive emissions (weight of emissions per weight of material processed).

With the exceptions noted below, two methods were used to measure styrene emissions. A heated Tedlar™ bag sampler was used to obtain an integrated sample of the contaminated air exiting a representative point in each process exhaust vent (EPA Reference Method 18).^{5,8} Concurrently, styrene emissions were measured on a continuous basis using a Total Hydrocarbon Analyzer (THC) equipped with Flame Ionization Detectors (FIDs). Sample times ranged from 40 to 45 minutes, typically the time required to spray eight to ten molds. Sample times were dictated by the plant production rate and the time available for sampling during a particular period of spraying.

Test Matrix

Fifteen locations were sampled for styrene. Eleven of these locations were roof vents from spray booths (seven booths were in use throughout the evaluation while the other four were used only for building ventilation), while the four other locations were exhaust fans located on the side of the building. Three exhaust fans were devoted to area ventilation for the building and one exhaust fan was used to provide ventilation for the resin mixing room.

As noted in Section 1, because production was carried out only four days per week (Monday through Thursday) instead of five days per week, one less day of testing was available than was scheduled. The original test schedule called for one day of setup (Monday), four days of testing (Tuesday through Friday), a weekend off, and the next week to be devoted to the evaluation of a pilot-scale liquid chemical scrubber with Monday being a setup day. Unfortunately, it was not known that the plant was on a four-day production schedule until Monday, June 14. On that day, after consulting with the EPA Project Officer, it was decided that to obtain the maximum amount of reliable data during the week of June 14, EPA Method 18 sampling would be focused on the seven active spray booths and that styrene emissions from non-active booths and building exhaust fans (including the resin mixing

room exhaust fan) would be measured with THC analyzers only. Because these measurements could not all be completed during the week of June 14, THC sampling of exhaust fan emissions was carried out on Monday of the following week (while preparations were underway to begin the evaluation of the liquid chemical scrubber). No more time could be taken from the evaluation of the liquid chemical scrubber because the following week was also to be a four-day work week with one less day of sampling than was expected. With the permission of the EPA Project Officer, headspace samples from styrene storage tanks were also not taken because the vats of styrene containing mix are open at their tops, so it was decided that a sample would be taken from the air exiting the resin mix room. Table 2 shows the sampling and analytical test matrix that was used for this testing. Details of the sampling and analytical procedures used for this evaluation are presented in Section 3.

ELJER PLUMBINGWARE FACILITY

The Eljer Plumbingware facility, diagrammatically shown in Figure 1, is located in Wilson, North Carolina. In this figure the location of each process vent is indicated. There are a total of fifteen vents where air is exhausted. Eleven of these vents are from spray booths, seven of which were used for spraying during this test. Three large fans shown on Figure 1 are used to provide a continuous source of outside ventilation air to the plant. During this testing, three booths were not used (marked as "unused" in Figure 1) and the air exhaust on these booths was closed off (normally, all fifteen vents are used throughout the day). Ventilation air is turned on approximately 15 minutes before the workday starts and is shut off approximately fifteen minutes after the workday ends.

Table 2. Eljer Plumbingware Test Matrix

Sample Location	No. of Runs	Sample Type	Procedure	Sample Duration	Analysis Method
Gel Coat Booth #1	1	Gas Velocity	Method 1-2	30 min.	Pitot
	4	Styrene	Method 18	45 min.	GC/FID
	5	Styrene/Gas Velocity	THC Analyzer	45 min.	THC/FID, Pitot
Gel Coat Booth #2	4	Gas Velocity	Method 1-2	30 min.	Pitot
	4	Styrene	Method 18	45 min.	GC/FID
	6	Styrene/Gas Velocity	THC Analyzer	45 min.	THC/FID, Pitot
Gel Coat Booth #3	2	Gas Velocity	Method 1-2	30 min.	Pitot
	3	Styrene	Method 18	45 min.	GC/FID
	3	Styrene/Gas Velocity	THC Analyzer	45 min.	THC/FID, Pitot
Lay-Up Booth #1	1	Gas Velocity	Method 1-2	30 min.	Pitot
	4	Styrene	Method 18	45 min.	GC/FID
	5	Styrene/Gas Velocity	THC Analyzer	45 min.	THC/FID, Pitot
Lay-Up Booth #2	1	Gas Velocity	Method 1-2	30 min.	Pitot
	3	Styrene	Method 18	45 min.	GC/FID
	3	Styrene/Gas Velocity	THC Analyzer	45 min.	THC/FID, Pitot
Lay-Up Booth #3	1	Gas Velocity	Method 1-2	30 min.	Pitot
	3	Styrene	Method 18	45 min.	GC/FID
	3	Styrene/Gas Velocity	THC Analyzer	45 min.	THC/FID, Pitot
Lay-Up Booth #4	2	Gas Velocity	Method 1-2	30 min.	Pitot
	1	Styrene/Gas Velocity	THC Analyzer	33 min.	THC/FID, Pitot
Lay-Up Booth #5	2	Gas Velocity	Method 1-2	30 min.	Pitot
	1	Styrene/Gas Velocity	THC Analyzer	12 min.	THC/FID, Pitot
Lay-Up Booth #6	2	Gas Velocity	Method 1-2	30 min.	Pitot
	1	Styrene/Gas Velocity	THC Analyzer	10 min.	THC/FID, Pitot
Back-Up Booth #1	2	Gas Velocity	Method 1-2	30 min.	Pitot
	4	Styrene	Method 18	45 min.	GC/FID
	5	Styrene/Gas Velocity	THC Analyzer	45 min.	THC/FID, Pitot
Back-Up Booth #2	2	Gas Velocity	Method 1-2	30 min.	Volumetric
	1	Styrene/Gas Velocity	THC Analyzer	10 min.	THC/FID
Exhaust Fan #1	1	Gas Velocity	Velocity Meter	30 min.	Volumetric
	1	Styrene	THC Analyzer	18 min.	THC/FID
Exhaust Fan #2	1	Gas Velocity	Velocity Meter	30 min.	Volumetric
	1	Styrene	THC Analyzer	33 min.	THC/FID
Exhaust Fan #3	1	Gas Velocity	Velocity Meter	30 min.	Volumetric
	1	Styrene	THC Analyzer	31 min.	THC/FID
Exhaust Fan, Resin Mixing Room	1	Gas Velocity	Velocity Meter	30 min.	Volumetric
	1	Styrene	THC Analyzer	14 min.	THC/FID

* No active spraying was carried out in these booths during the test period. Used for ventilation only.

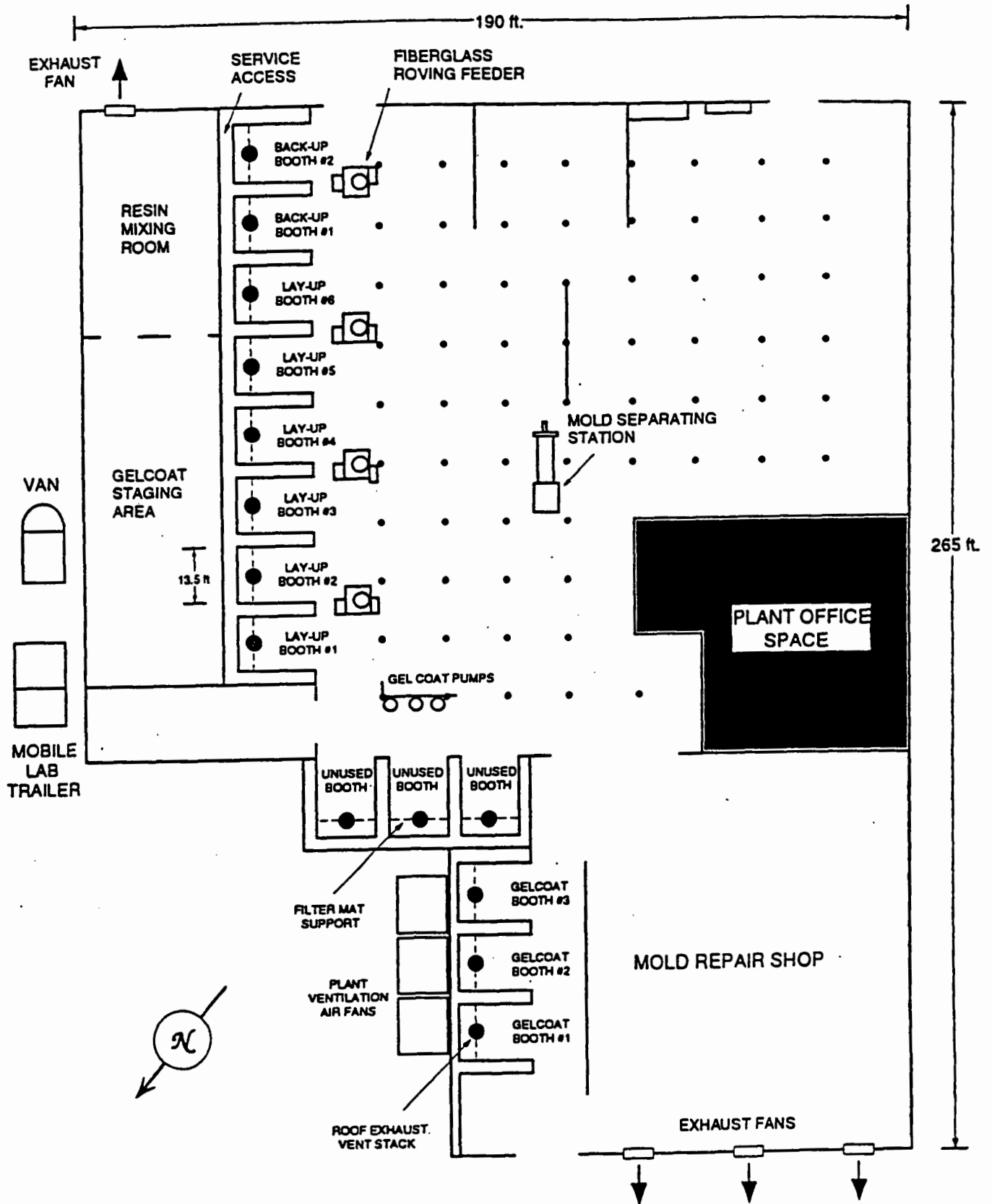


Figure 1. Layout of Eljer Plumbingware Facility

During this evaluation, the workday started at 0700. One-half hour breaks in production occurred at 1000 hours (morning break) and 1200 hours (lunch break). The workday ended at 1400. Thus, during a typical day of testing, all ventilation fans ran for 7.5 hours while three periods of mold spraying took place: 0700 to 1000, 1030 to 1200, and 1230 to 1400, accounting for six hours of actual spraying.

Each stage of manufacture except for mold separation or "pulling" is carried out in a spray booth. At the Eljer facility the spray booths were not constructed in place but are prefabricated units manufactured by Binks, Inc. The available volume in each spray booth is comprised of a height of about 3.05 m (10 ft), a width of about 4.11 m (13.5 ft), and a depth of about 3.66 m (12 ft). The booths are approximately 1 m deeper but 3.66 m back from the mouth of the booth an expanded metal grate is mounted across the width and height of the booth on which a large sheet of air conditioning-type filter material is mounted. The filter material is usually changed every other day. While these filters appear quite dirty when they are removed, the results of velocity traverses made at the exit vent of a booth before and after the filter material was replaced showed that air flow was essentially unaffected by a clean or dirty filter.

Each spray booth is continuously vented with air from the interior of the plant that is pulled into the booth entrance, through the filter mat, and a five-blade fan unit mounted approximately 2 m below the roof of the building. Air pulled into the fan exits vertically through a 0.91 m (3 ft) diameter stack mounted on the roof of the facility. Each exhaust fan has a nominal rated flow of 411 m³/min (14,500 acfm). During testing, fan capacities of from 353.5 to 427.9 m³/min (dry, referenced to 20°C) were measured.

There are three distinct manufacturing steps that are required to produce a fiberglass shower stall or bath tub at the Eljer facility. First, a prepared mold is mounted on a cart and wheeled into one of the three gel coat spray booths located near the mold repair shop. In the spray booth, the mold and cart are designed to slide onto the arm of a permanently mounted pedestal assembly that can be hydraulically elevated above the floor of the spray booth. The mold and cart are also designed to rotate on the arm of the pedestal so that all parts of the mold are accessible for spraying. This mounting system is duplicated in every spray booth at the Eljer facility.

Gel coat is a mixture of styrene monomer, polyester resin, and pigment (chromatographic analysis, 32.2% styrene) and is purchased as a prepared mix in 55 gallon drums. During this test, the gel coat mix contained no additive to suppress styrene vapor emissions. At the time of this test at least four colors of pigment were observed: white, off white, pink, and blue. However, plant records only keep track of white and colored gel coat usage.

About two to three minutes are required to coat a bath tub mold (approximately 2.5 m²) with gel coat and about five minutes are required to coat a large shower stall mold (7-8 m²) with gel coat. After spraying is completed, the mold is oriented upright and the pedestal is lowered until the wheeled cart mounted to the mold contacts the floor. The mold and its attached cart are then wheeled out of the booth to await the next stage of manufacture. Between each stage of manufacture the coated mold is set aside to cure and harden for about an hour. Curing generates heat, so there is a time interval between sprayings to allow the coated mold to cool.

The second stage of manufacture is called the "first lay-up" or "initial laminating" step and occurs in two parts. In this stage, the mold is conveyed to one of the first lay-up booths and, as with the first step of manufacture, mounted on a pedestal and prepared for spraying. The mix sprayed in this stage is composed of a powdered inert filler added to a mixture of styrene monomer and polyester resin to form a slurry that contains approximately 50% solids (chromatographic analysis, 21.4% styrene). The lay-up mix is prepared in the resin mix room shown in Figure 1 and is pumped to the point of delivery.

Two coats of this slurry are sprayed onto the mold and during the spraying operation, chopped fiberglass roving (3 to 4 cm long) is also blown at about a 30° angle into the stream of spray as it exits the spray nozzle. The spray mixes with the strands of chopped fiberglass and forms a entangled mat of resin impregnated fiberglass on the surface of the mold. The inert filler and the chopped fiberglass help provide structural support to the finished product. Between sprayings, the mold is left in the booth while from two to four workers quickly compact and flatten the matted surface of the mold with small, hand-held rollers. After the second spraying, the mold is wheeled from the booth and rolled again. The total time for both sprayings usually takes two to three minutes and rolling can take another one to two minutes. However, because one person is used to operate the sprayer in the three lay-up booths, the time between sprayings averages from seven to ten minutes while other molds are being sprayed in the other lay-up

booths. As with the first stage of manufacture, this step is brief and requires only three to five minutes to complete. When this step is completed the coated mold is once again set aside to cure.

The third, and final, spraying step is called the "second lay-up" or "back up" step and takes place in one of the two second lay-up booths shown in the upper left corner of Figure 1 (Back-Up Booth #1 or Back-Up Booth #2). During this evaluation, only back-up booth #1 was used. Like the lay-up step, this operation is carried out in two parts with two spraying steps. In this step, a blend of powdered inert filler (incorporating a fire retardant) is added to a mixture of styrene monomer and polyester resin to form a slurry that contains approximately 50% solids (chromatographic analysis, 20.9% styrene). As with the lay-up mix, the back-up mix is prepared in the resin mix room shown in Figure 1 and is pumped to the point of delivery.

The back-up mixture is also sprayed with chopped fiberglass fibers and forms the final two layers of the product. As with the second stage of manufacture, the mold is first moved into the back-up booth where a fresh layer of the back-up slurry/chopped fiberglass mix is sprayed onto the mold. The mold is then moved out in front of the booth where precut chipboard and corrugated paper supports are pressed and molded into the wet slurry/fiberglass layer on the sides and bottom of the mold. The mold is then moved back into the booth for a final spraying that covers all of the chipboard and heavy corrugated paper supports. After the mold emerges from the back-up booth for the second time it is manually rolled and set aside to cure for the last time.

Two molds are usually worked on at a time. Thus, while the supporting layer of chip board and corrugated paper is applied to one mold, another mold is being sprayed with its first layer of back-up mix. When the second mold is moved back into the booth for its final spraying, the first mold has its supporting layer of chip board and corrugated paper applied. This step is brief and requires only seven to ten minutes to complete two molds.

The last phase of manufacture is "pulling" or separation of the mold from the completed shower stall or bath tub. After the finished fiberglass piece is trimmed and inspected it is prepared for shipment.

During the time of the emissions testing, on a daily basis, this facility consumed approximately 500 kg gel coat mix and approximately 4000 kg of lay-up mix and back-up mix. On the basis of a four-day work week, which was typical for that time, and a 50-week work year, yearly gel coat mix

consumption would be approximately 100,000 kg, and yearly consumption of lay-up and back-up mix would be approximately 800,000 kg.

SAMPLING LOCATIONS

Two types of sampling locations were encountered in this evaluation. The first type of sampling location was located on the roof of the facility and consisted of a 0.91 m (3 ft) diameter stack that extended approximately 1.5 m (5 ft) above the surface of the roof. Eleven such stacks are used to convey vent air to the outside from the eleven spray booths with operating exhaust fans. Moveable split circular doors are positioned approximately 0.3 m (1 ft) below the top of each stack. These split doors are designed so that when the exhaust fan feeding the stack is turned on, the doors fold together, up and out of the way, kept open by the outwardly moving air stream. When the exhaust fan feeding the stack is turned off, the doors close to prevent the entrance of rain or vermin. The actual exhaust fan for each stack is located approximately 2 m (6.6 ft) below roof level. The fans typically have five blades. Figure 2 shows the overall arrangement for one of these sampling locations.

As Figure 2 shows, because of the eductor-type shroud that is mounted near the surface of the roof, and because of the split door covers, it was necessary to conduct all sampling from as close to the top of the roof as was possible. Below the eductor-type shroud and above the rain cap, two small 2.5 cm (1 in.) holes were drilled in the side of each stack at a 90° angle to each other, just large enough to allow the entry of an s-type pitot or Method 18 sampling probe. Because the vents were at essentially atmospheric pressure, no significant amount of air entered or was lost through these small ports. The ports were covered over at the end of the evaluation.

The second type of sampling location was at the exhaust of a three or four-bladed exhaust fan on the side of the building shown in Figure 1, about 3 m (10 ft) above the ground. These fans were protected from the elements by horizontal louvers on the discharge side of the fan that close when the fan is turned off, but are kept open by air exiting the fan when it is turned on. Because the louvers tended to oscillate from nearly fully open to approximately 75% open while they operated, the louvers had to be held fully open to be able to measure the velocity of the air exiting any one of these fans. Even so, because these fans operate with no stack to straighten or direct their exhaust, air flow is very uneven.

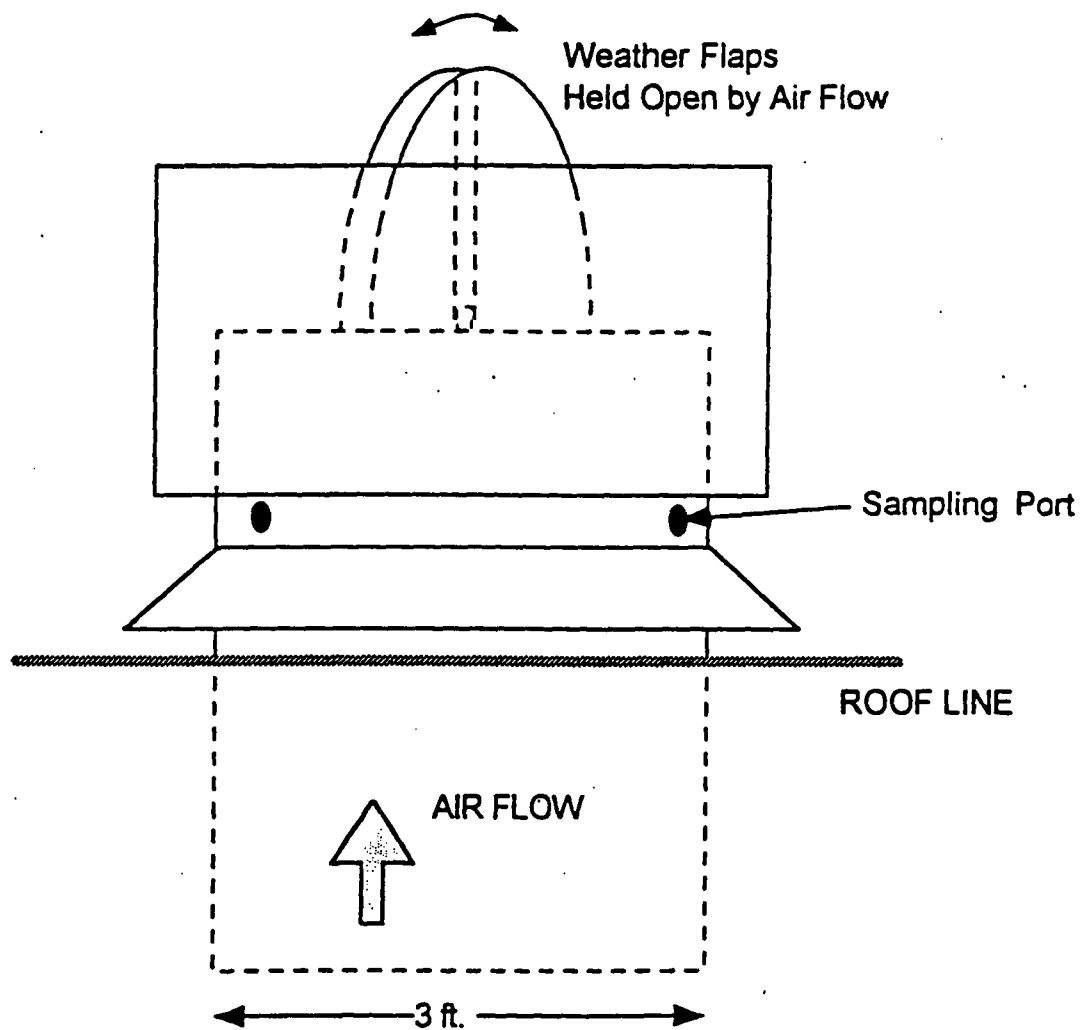


Figure 2. Overall Arrangement for Roof Sampling Locations.

Three exhaust fans were located on the northwest side of the building. Another fan of this type was located on the southeast side of the building and was used to ventilate the resin mixing room. Air velocity was measured with a direct reading velocity meter that was checked against the s-pitot used at the spray booth exhausts for air flow measurement.

SECTION 3

SAMPLING AND ANALYTICAL PROCEDURES

The sampling and analytical procedures used for this evaluation incorporated the most recent revisions of the published EPA methods, where applicable. In this section, descriptions of each sampling and analytical method that was used in this evaluation are presented.

In order to meet the test objectives in an expedient manner, a trailer housing a mobile laboratory was set up on site. All gas chromatographic (GC) analysis of the integrated Tedlar bag samples for styrene were performed there. This trailer was also equipped for sampling two separate emissions sources with THC monitors.⁷ The trailer was supplied by DEECO, Inc. of Cary, NC who also provided personnel to conduct the Method 18 sampling and GC-FID analysis. The mobile laboratory was located on the northeastern side of the building, outside, next to the gel coat staging area. In addition to the mobile laboratory, a second vehicle, a van, was equipped for THC sampling and was used in this evaluation and for the evaluation of a liquid chemical scrubber during the week following this testing. The van was located in front of the mobile laboratory, along the northeastern side of the building.

Electrical power was provided to the mobile laboratory from plant service (a 220 VAC line) through cabling supplied by Southern Research. Electrical power was connected and disconnected by a local electrical contractor familiar with the plant power system. Electrical power to the van for the THC analyzers and ancillary electrical equipment was obtained from one leg of the 220 VAC line that fed the mobile laboratory. Power for roof top sampling was carried by heavy-duty extension cords from a power distribution center installed by the electrical contractor for the duration of the test.

PLANT PROCESS INFORMATION

Eljer Plumbingware provided plant raw material usage records for the three days during which spray booth samples were taken. These records are reproduced in Table 3. These data gave raw material usage in terms of kilograms of product used in each phase of manufacture and in

Table 3. Plant Raw Material Consumption, June 15-17, 1993*

Item	Units	6/15/93	6/16/93	6/17/93
Gel Coat Mix (32.2% Styrene*)				
Area Sprayed	m ²	664.6	646.0	653.0
White Mix	kg	290.8	295.7	286.2
Colored Mix	kg	197.3	220.4	226.8
MEKP	kg	7.3	7.7	7.7
Total	kg	495.3	523.9	520.7
Lay-Up Mix (21.4% Styrene*)				
Area Sprayed	m ²	640.5	642.1	652.1
Resin (incl. styrene)	kg	958.0	909.9	923.5
Inert Filler	kg	1272.3	1208.8	1226.5
Pigment	kg	1.8	1.4	1.4
Vapor Suppressant	kg	5.0	4.5	4.5
MEKP	kg	27.7	26.3	26.8
Fiberglass Roving	kg	306.2	306.2	349.3
Total	kg	2571.0	2457.1	2532.0
Back-Up Mix (20.9% Styrene*)				
Area Sprayed	m ²	640.5	642.1	652.1
Resin (incl. styrene)	kg	775.2	721.2	716.2
Inert Filler	kg	1166.6	1085.4	1077.7
Pigment	kg	1.4	1.4	1.4
Vapor Suppressant	kg	4.1	3.6	3.6
MEKP	kg	29.0	27.2	26.8
Fiberglass Roving	kg	163.3	161.9	165.6
Total	kg	2139.6	2000.8	1991.3

* Results for sample obtained on 6/22/93 at 1020 hours.

kilograms of product used per square foot of mold sprayed. The total area of mold that was sprayed in each phase of manufacture was also provided as part of the daily record.

To relate the emissions data taken at each active spray booth to raw material usage, records were kept of the area of molds that were sprayed in each active booth while sampling was underway. Because plant production records do not track where a mold was sprayed, portable video cameras were used to record the spraying activity that took place in a particular spray booth while the air exhausted from that booth was being sampled. Afterwards, by inspecting the video record, mold types could be identified and, with the help of catalog data sheets provided by Eljer Plumbingware, the total mold area sprayed could be determined for each period of sampling. In this way, styrene emissions per unit area of mold sprayed could be determined to compare with styrene use per unit area of mold sprayed.

Unfortunately, one video camera failed partway through the test and two data sets from the same spray booth were lost (gel coat booth #2). Data from two other spray booths were lost when one camera was inadvertently pointed at the wrong spray booth (lay-up booth #3 instead of lay-up booth #2) and when plant production was shifted away from one booth so that no molds were sprayed during the time that booth was sampled (gel coat booth #1).

EPA METHOD 18 SAMPLING

Samples for on-site analysis of styrene content were collected using EPA Method 18, according to Section 7.1.1 of the method: Integrated Bag Sampling and Analysis, Evacuated Container Sampling Procedure.⁶ Time integrated samples were collected for a typical collection time of 45 minutes by drawing spray booth exhaust air into new 15 liter Tedlar or Teflon bags at constant sampling rates. With one exception, samples were collected in triplicate or quadruplicate at the locations described in Table 2. Each sample was analyzed on site by gas chromatography utilizing a flame ionization detector (GC/FID). Stack parameters of velocity and flow rate were determined by Methods 1-2.

Method 18 Sampling Equipment

Styrene-containing samples of spray booth exhaust were collected in evacuated Tedlar and Teflon bags. The sampling train consisted of a heated Teflon probe and sampling line, heated leakproof rigid sampling container, and VOST-train sampling boxes with sampling pump and dry gas meters. Constant sampling rates were used, typically 0.25 liter/minute. To prepare for sampling, Tedlar or Teflon bags were blanked with dry air, evacuated, and sealed into the sampling containers.

All bags were heated to 11°C (20°F) above ambient to minimize styrene loss. This temperature was chosen because rooftop temperatures averaged about 38°C (100°F) during most testing. The Teflon probes and sampling lines were also maintained at 49°C (120°F). Thus, bags were evacuated, installed in the sampling containers, and preheated to 49°C (120°F) before being taken to the sampling location. Before, during, and after sampling, and until they were analyzed, the 15 liter Tedlar bags were maintained at 49°C (120°F) within the sampling container.

Method 18 Sampling Procedures

The order of testing was determined by spray booth availability and distance from the mobile laboratory. Testing started with gel coat booths 1 through 3 which were the furthest away from the mobile laboratory. Lay-Up booths 1 through 3 were sampled next, then Back-Up booth #1 and any other spray booths that needed to be repeated.

To prepare for sampling, in the mobile laboratory, evacuated Tedlar or Teflon bags were placed in the rigid, leakproof sampling container and the inlet of the bag was connected to one of two Swagelock® fittings mounted in the top of the container. The lid was placed on the container and sealed. At this point the heating jacket on the container was allowed to bring the container and its bag to 49°C (120°F). When the container had stabilized at 49°C (120°F), it was transported to the roof of the facility. On the roof, each sample container was leak checked, and the heated probe and sample line were attached to the sample container. The probe was placed at a point where the local velocity was approximately

equal to the average velocity measured for the stack, as close to the center of the stack as was possible, and the bag and sample line were conditioned with stack gas by filling and evacuating the bag three times in succession. Sampling began and pertinent times and sampling parameters were entered on the appropriate run sheet. Sampling continued for 45 minutes with the exception of four runs that were cut 5 minutes short because spraying in a particular booth had temporarily ceased.

When sampling was completed, the heated sampling container and Tedlar or Teflon bag was returned to the mobile laboratory for analysis. For analysis, contents of the heated bag were sampled directly by the GC/FID in the mobile laboratory within one to two hours after sampling was completed. The bag was then removed and discarded while a new bag was fitted into the rigid sample container and allowed to heat.

Method 18 Styrene Analysis

Samples were analyzed by GC/FID in the on-site mobile laboratory. The GC/FID instrument conditions were as follows:

- Shimadzu GC-14A Gas Chromatograph with 0.5 ml sample loop.
- Column - 30 m long megabore column (0.53 mm I.D) 1 μ m film thickness, Restek RTX-1 (Equivalent to J&W DB-1)
- Detector - Flame Ionization
- Temperature program - isothermal at 100°C
- Integrator - Shimadzu CR-501.

To calibrate the GC-FID, the sample loop was flushed with a standard and then injected into the GC-FID and the area count was measured by the integrator. This was repeated for each standard. A

calibration curve was developed by performing a least squares fit using the concentrations and corresponding area counts of the standards. A calibration curve was developed at the beginning of each day of sampling.

Initially, it was planned to calibrate the GC with styrene standards prepared according to Section 6.2.2.2 of Method 18 (Liquid Injection Technique). However, at the time of this test, the equipment required to generate such styrene standards on site was not available. Therefore, precision of the GC-FID was established by repetitive sampling of styrene standards contained in commercially available compressed gas cylinders. Immediately before this test, two bottles each of low and mid-range styrene calibration standards (nominal 5 and 50 ppmv of styrene in nitrogen) were ordered from Matheson Gas Products. When received, the styrene concentrations were certified by vendor analysis to be 3 ppmv (for both bottles of nominal 5 ppmv styrene gas) and 52 and 54 ppmv (for the two bottles of nominal 50 ppmv styrene calibration gas). For a high styrene calibration standard, an unused bottle of nominal 200 ppmv styrene calibration gas (in nitrogen) left over from a previous EPA evaluation carried out at the Eljer facility in October 1992 was used. The concentration of styrene in this cylinder was certified by Matheson Gas Products to be 195 ppmv when it was received in October 1992.

Time integrated bag samples were analyzed in the same manner by flushing the sample loop, injecting the sample, noting the retention time, and measuring the area count. Identification of styrene was based on retention time established by the calibration standards. The area count was converted into a concentration using the least squares calibration developed with the calibration standards. Each sample was analyzed in duplicate. No interferences were anticipated due to the fact that no other chemicals except MEKP are used in the manufacturing process. MEKP is used in very small quantities relative to the amount of styrene-containing mix sprayed (1.1 to 1.5% by weight) and would not be detected by the GC/FID or the THC analyzers. Also, during a previous test conducted at the Eljer facility, GC-FID analysis of EPA Method 18 samples obtained using the adsorption tube procedure showed only the presence of styrene in the air exhausted from gel-coat, lay-up, and back-up spray booths.⁸

At the time of testing the EPA Project Officer decided against requiring a separate analysis of an appropriate styrene audit material. However, after sampling was over, inconsistent styrene concentrations from concurrent GC/FID and THC measurements suggested that it would be appropriate to request that an audit sample be supplied for analysis. The audit cylinder was analyzed using the Absorption Tube Procedure of Method 18 and the results of this analysis was found to be well within $\pm 10\%$ of the verified concentration. Unfortunately, this showed that there was substantial error in the factory analyses of the standard gas mixtures of styrene used for field calibration, necessitating an overall correction of the results. Subsequently, it was determined from THC analyses using a THC analyzer that had been calibrated with the EPA styrene Audit Standard that the calibration gas standards obtained from Matheson Gas Products actually contained 2.2, 39.4 (Matheson-certified 54 ppmv), and 170.8 ppmv of styrene, respectively (see Appendix A). As is also shown in Appendix A, the Matheson-certified 52 ppmv styrene cylinder was determined by EPA Method 18 analysis (adsorption tube procedure) to contain 39.1 ppmv of styrene. The manner in which these errors in styrene concentration were detected and the effort that was required to correct the data taken in the field are detailed in the Quality Control Evaluation Report in Appendix A.

SAMPLING WITH THC ANALYZERS

JUM Instruments Model VE-7 total hydrocarbon (THC) analyzers were used to monitor styrene emissions from active spray booths during time periods when Method 18 sampling was conducted at these spray booths. In addition, the THC analyzers were used to monitor styrene emissions from otherwise active spray booths during mid-morning breaks and lunch breaks and to monitor styrene emissions from all other points of ventilation air exhaust.

Four JUM THC analyzers were used for this sampling. Two of the THC analyzers were associated with the GC/FID system in the mobile laboratory. The other two THC analyzers were kept in the van and were used to corroborate data taken with the THC analyzers in the mobile laboratory. Figure 3 shows how these analyzers were configured. As is shown in this figure, two long sampling hoses were

used to convey a sample of exhaust air from a process vent to one pair of THC analyzers. These 0.635 cm (0.25 in.) outside diameter sample lines were made of Teflon and were heated to approximately 66°C (150°F) and were 22.9 m (75 ft) long. At the flow rates used for sampling, transit time through the lines averaged between 43 and 51 seconds.

Data from two of the THC analyzers, those in the mobile laboratory, were recorded on a dedicated chart recorder and logged on a PC-based data acquisition system (DAS) developed by DEECO, Inc.⁷ Output from each THC analyzer was averaged over a period of one minute and the one minute averages were recorded by the data logger. The chart recorder recorded instrumental output on a continuous basis. A S-type pitot probe with a K-type thermocouple was positioned in the stack in close proximity to the Method 18 sampling probe and the probe used for the THC analyzers. One minute averages of the pressure drop across the S-type pitot probe and the temperature recorded by the K-type thermocouple attached to the probe were also logged on datalogger. In this manner, if the flow rate of air exiting a particular spray booth was observed to change or fluctuate significantly, the run could be aborted. Overall, flow rates through a given spray booth exhaust were observed to vary insignificantly over time and no runs had to be aborted because of unstable exhaust flow.

The two THC analyzers in the mobile laboratory were calibrated with 850 ppm $\pm 1\%$ propane in the morning and in the afternoon and instrument zero was verified with hydrocarbon-free air (less than 0.1 ppm THC). To be able to develop comparisons with the other two THC analyzers that were calibrated with styrene, mid-range styrene calibration gas (nominal 50 ppmv) was also sampled by these instruments and the result was recorded. See the Quality Control Evaluation Report in Appendix A for details of this comparison. Data from the two THC analyzers in the van were logged on a separate DAS. This PC-based DAS recorded instrumental output once a second and logged the values on a floppy disk along with local time. Outputs from these THC analyzers were also recorded on a two-channel chart recorder which was annotated and became part of the experimental record.

The two analyzers in the van were calibrated before sampling started in the morning, and at the mid-morning break with mid-range (nominal 50 ppmv) calibration gas and were also checked for linearity

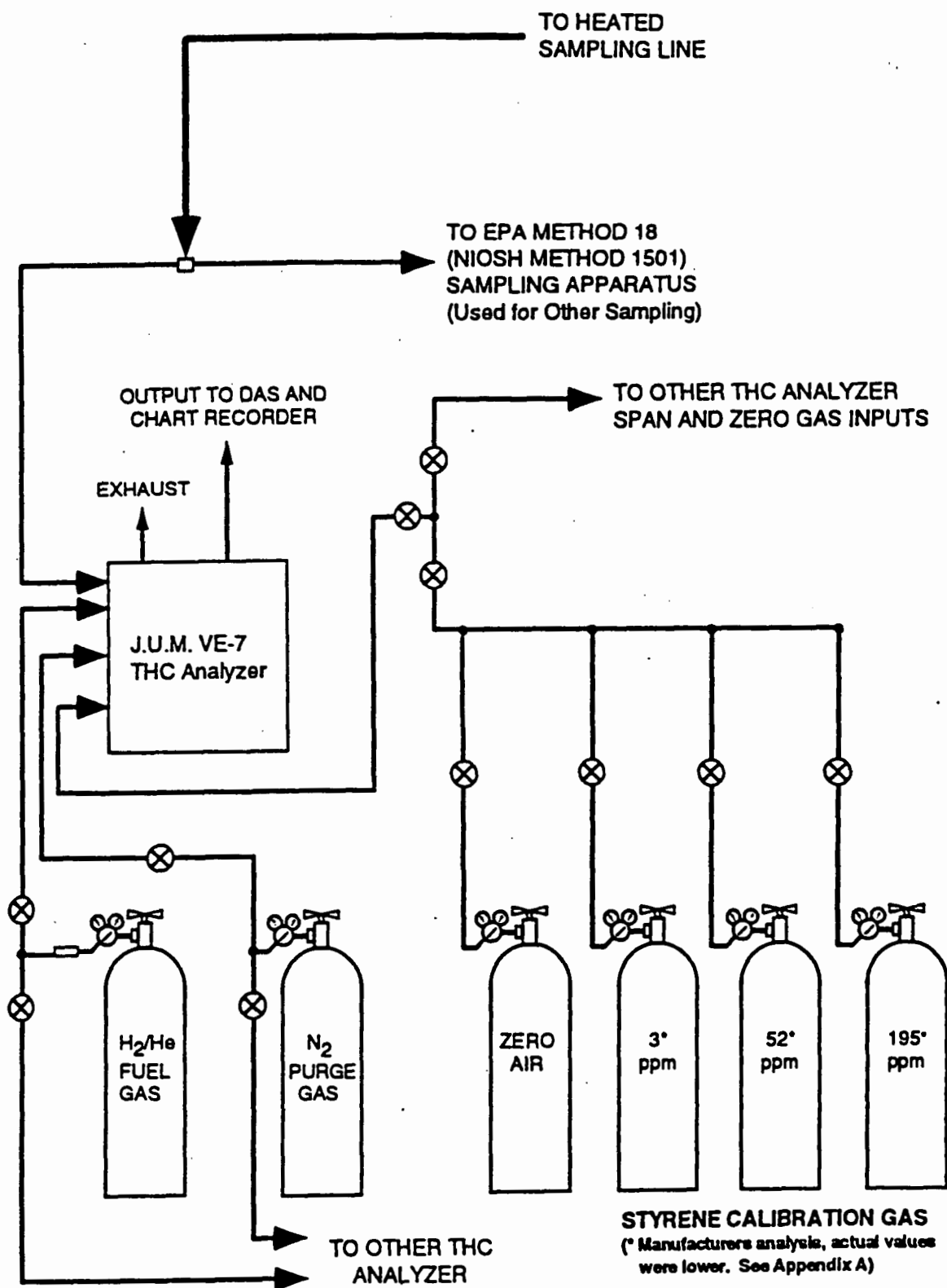


Figure 3. Equipment Arrangement Used for Sampling with THC Analyzers

with low (nominal 5 ppmv) and high-range (nominal 200 ppmv) styrene calibration standards. The calibration was also checked at the end of the day. As part of each calibration check, instrument zero was verified with hydrocarbon-free air (less than 0.1 ppm THC). A 10.7 ppm propane standard was also used to determine an instrumental response for propane.

VOLUMETRIC FLOW RATE DETERMINATION

For spray booth exhausts, volumetric flow was determined according to EPA Method 2.⁶ A type K thermocouple and S-type pitot probe were used to determine flue gas temperature, and velocity, respectively. EPA Method 1 was used to determine the number of traverse points.⁶ Parameters measured included pitot pressure drop, stack temperature, static, and barometric pressure. A computer program was used to calculate the average velocity.

Stack exhaust gas was assumed to be ambient air. Throughout the test relative humidity averaged approximately 60% (monitored on-site with a relative humidity sensor, Cole Parmer Model 3310-40). At typical plant air temperatures (27°C or 80°F) this corresponds to 2% water vapor in the air, the value that was used for dry gas corrections.

The other ventilation exhausts were three or four-bladed exhaust fans. Because of the very uneven air flows and the absence of a flow straightening exhaust stack, it was essentially impossible to determine the location of suitable traverse points or to make measurements with an s-type pitot probe. Thus, with the permission of the EPA Project Officer, a direct reading air velocity meter (Air-Neotronics Model 50-4) with a long enough averaging time to suppress the effects of buffeting from the fan exhaust was used to determine an average velocity. The direct reading air velocity meter was checked against the s-type pitot probe in one of the spray booth exhaust vents.

SECTION 4

RESULTS

Emission factors were calculated from emission rates determined from THC analyzer and Method 18 sampling and knowledge of the amount of styrene used in each stage of manufacture at the Eljer facility (from production records for each day of testing, shown in Table 3). Knowledge of the total of area sprayed during Method 18 sampling (from inspection of videotapes made of spraying carried out in the booth being sampled to identify the type and surface area of mold sprayed) provided the amount of styrene expended per square meter of mold sprayed. Comparison of the styrene emission rate determined from THC analyzer and Method 18 sampling at the exhaust of a given spray booth with the amount of styrene sprayed yielded the emission rate for that part of the manufacturing process.

Thus, if M_s is the mass of styrene sprayed per square foot of mold area for a given phase of the spraying operation (supplied from plant production records and analysis of samples of mix from each spraying operation) and A_i is the surface area of the i th mold sprayed, the mass of styrene sprayed during the spraying of that mold, M_i , is equal to the product of M_s and A_i :

$$M_i = M_s \cdot A_i \quad (1)$$

If during a period of time, T_s , when THC analyzer or Method 18 sampling was conducted, n molds were sprayed, the total mass of styrene sprayed, M_T was:

$$M_T = M_s \sum_{i=1}^n A_i \quad (2)$$

Now, if C_{SB} is the concentration of styrene measured at the exhaust stack of the active spray booth under test (from the THC analyzer or Method 18 measurement), and if the average air flow rate through the booth under test is Q_{SB} , then the rate at which gaseous styrene is emitted through the spray booth exhaust vent (emission rate over the time of the Method 18 measurement) is:

$$E_{SB} = C_{SB} \cdot Q_{SB} \quad (3)$$

and the total mass of styrene emitted during the time T_s is:

$$M_{SB} = E_{SB} \cdot T_s \quad (4)$$

It should be noted that this calculation presumes that none of the styrene sprayed in a given spray booth escaped through the front of the booth into the plant. There are two reasons why this assumption is warranted: First, all spraying is directed into the booth, i.e. in reviewing the videotape record made to identify which molds were sprayed while sampling was carried out in a particular booth, the operator of the spray gun was never observed to direct the spray gun toward the mouth of the booth. Second, the net air velocity into the booth (across the mouth of the booth) ranged from 0.47 to 0.57 m/s, which should be great enough to capture all styrene vapor generated in the booth.

Indeed, because styrene emissions associated with spraying do not escape from spray booths into the plant, some styrene emissions from other parts of the manufacturing process must be captured by air being swept into the spray booths. At the Eljer facility (and perhaps at other similar facilities), molds that have been sprayed are frequently left near the mouths of spray booths where spraying is in progress. Thus, styrene evolved from a curing mold can be captured by an nearby spray booth. While this is probably not a common occurrence for gel coat booths at the Eljer facility (because of limited space in front of these booths), it is an integral part of the manufacturing process for the latter two stages of spraying. In fact, at any one time, it is common for as many fifteen molds to be in various stages of manufacture in the general vicinity of the lay-up and back-up booths. Also, molds are generally left in a

lay-up booth between sprayings where the surface of the mold is rolled flat. In AP-42 it is noted that styrene emissions are increased by such manual rolling.¹

Thus, the concentration of styrene measured at the exhaust of a given active spray booth, C_{SB} , is actually the sum of the concentration of styrene vapor emitted in the spray booth, C_S , and the concentration of styrene vapor swept into the spray booth from the area adjacent to the spray booth, C_P :

$$C_{SB} = C_S + C_P \quad (5)$$

and equation (3) should be written as:

$$E_{SB} = (C_S + C_P) \cdot Q_{SB} \quad (6)$$

Then the emission factor, F_{SB} , for the spray booth under test is the ratio of the amount of styrene emitted, M_{SB} , from equation (4) to the amount of styrene sprayed, M_T , from equation (2):

$$F_{SB} = \frac{M_{SB}}{M_T} \quad (7)$$

Styrene emissions not captured by the active spray booth exhaust fans (styrene evolved from recently sprayed molds and from open resin mixing tanks) were determined in a similar manner. During periods of normal production styrene emissions were measured at every point where plant ventilation air was exhausted to the atmosphere (this included four ventilation exhaust fans and four spray booths that were not in use but whose exhaust fans were kept running throughout the day). Also, during the two daily breaks in production (morning break and lunch break), styrene emissions were measured at normally active spray booths where the exhaust fans were left running. Thus, for a given ventilation exhaust fan, unused spray booth, or inactive spray booth, if C_v is the concentration of styrene measured at the exhaust point under test (from the THC analyzer), and if the average air flow rate for this location is Q_v , then the rate at which gaseous styrene is emitted through a ventilation fan, an unused spray booth exhaust vent, or an inactive spray booth exhaust vent (mass emission rate over the time of the THC measurement) is:

$$E_{Vi} = C_{Vi} \cdot Q_{Vi} \quad (8)$$

Because these emissions are not directly tied to a mold surface area or stage of the production process, mass emissions per unit time were determined by equation (8), and extrapolated to a typical day of production using the amount of time spent spraying and the amount of time spent on break. Thus, if T_P is the total time spent spraying during the three periods of mold production and if T_B is the total time spent on break (morning break plus lunch break) then the total mass of styrene emitted from a given ventilation exhaust fan or unused spray booth is:

$$M_{Vi} = E_{Vi} \cdot (T_P + T_B) \quad (9)$$

and the total mass of styrene emitted from an inactive spray booth (during a break in production) is:

$$M_{ISBj} = E_{Vj} \cdot T_B \quad (10)$$

Thus, the emission factor, F_V , associated with styrene emissions not captured by the spray booth exhaust fans (from recently sprayed molds and from open resin mixing tanks) is the ratio of the total amount of styrene vented through the four ventilation exhaust fans and four unused spray booths and the seven inactive spray booths to the total amount of styrene sprayed during a given day of production, M_{ST} :

$$F_V = \frac{\left(\sum_{i=1}^8 M_{Vi} + \sum_{j=1}^7 M_{ISBj} \right)}{M_{ST}} \quad (11)$$

The amount of styrene sprayed on a given day, M_{ST} , was calculated from plant production records and chemical analysis (by chromatography) of samples of each mix sprayed (to determine styrene content). Knowledge of M_{ST} and the average mold area sprayed per day (from the three spraying operations) makes it possible to relate styrene emissions not captured by active spray booth exhaust fans to both the mass of styrene that was sprayed as well as total mold area.

The overall results of the sampling to determine styrene emissions are detailed below and the results of individual THC and EPA Method 18 runs are shown in Table 4. Styrene emissions per unit area of mold sprayed are presented in Table 5. Table 6 shows how styrene emissions were determined for styrene emissions not captured by the spray booth exhaust fans. Table 7 summarizes total mold surface area sprayed, plant raw material usage, and styrene use for each stage of manufacture for each day of testing. Table 8 combines the results shown in Tables 4 through 7 and presents average styrene emissions as a function of the area sprayed, the total mass that was sprayed, and the total amount of styrene that was sprayed. Finally, Table 9 shows relative styrene emissions for each stage of manufacture, including emissions not captured by spray booth exhaust fans.

As Tables 4 and 5 show, styrene emissions based on measurements with the THC analyzers were generally much greater than those determined by Method 18. The two techniques had been expected to produce comparable results. Indeed, it was felt that if one technique was to be biased toward a lower measurement, it would likely be the THC analyzers, because some styrene could be lost in the long heated sampling lines used to convey the ventilation air samples to the analyzers. Note, however, that Method 18 employs a complex procedure to obtain a time-averaged sample of an aerosol which must be transported to a GC-FID for analysis. In contrast, sampling with a THC analyzer is relatively straightforward and immediate. Nevertheless, as Table 8 shows (within the uncertainty of the data) that styrene emissions as determined from the two methods' data do overlap. It should be emphasized that because of the lack of multiple measurements, no uncertainty could be determined for styrene emissions not captured by spray booth exhaust fans (based only on THC analyzer data). Therefore, the uncertainties in Table 8 are *minimum* values. The lack of multiple measurements for such emissions is especially unfortunate because styrene emissions not captured by active spray booth exhaust fans are one of the largest sources of styrene emissions.

Research conducted subsequent to the above analysis of test results has also shown differences between EPA Method 18 measurements of styrene emissions and those using THC analyzers.^{9,10} However, the reason for these differences remains the subject of research. It has been suggested that in the Method

Table 4. Styrene Concentration and Emission Rate Summary for Eljer Plumbingware (June 1993)

Sampling Location	Date	Sampling Time Span	Vent Flow Rate (dscmm)	-----Styrene Concentration-----			-----Styrene Emission Rate-----		
				Lab THC (ppm)	Van THC (ppm)	Method 18 (ppm)	Lab THC (kg/hr)	Van THC (kg/hr)	Method 18 (kg/hr)
Gel Coat #1	6/15/93	0900-0945	374.3	45.4	N/A	21.5	4.413	N/A	2.093
		1030-1115	374.3	59.5	N/A	33.3	5.788	N/A	3.243
		1120-1205	374.3	N/A	59.7	39.2	N/A	5.806	3.810
	6/17/93	1245-1330	374.3	8.9	5.9	6.3	0.864	0.575	0.616
Gel Coat #2	6/15/93	0900-0945	373.6	60.5	N/A	24.7	5.869	N/A	2.399
		1030-1115	373.6	67.3	N/A	44.3	6.527	N/A	4.298
		1120-1205	373.6	N/A	65.2	62.3	N/A	6.331	6.046
	6/17/93	1245-1330	373.6	71.6	63.8	36.8	6.945	6.188	3.575
Gel Coat #3	6/16/93	0740-0825	362.2	60.9	N/A	39.7	5.732	N/A	3.735
		0830-0915	362.2	35.3	N/A	27.3	3.319	N/A	2.569
		0920-1005	362.2	49.4	51.1	41.4	4.647	4.813	3.986
Lay-Up #1	6/16/93	0740-0825	358.8	51.4	N/A	27.8	4.791	N/A	2.590
		0830-0915	358.8	49.5	N/A	30.5	4.618	N/A	2.835
		0920-1005	358.8	50.9	N/A	35.3	4.743	N/A	3.289
	6/17/93	1100-1145	358.8	42.0	35.2	29.7	3.911	3.282	2.772
Lay-Up #2	6/16/93	1030-1110	427.9	51.6	49.0	39.5	5.736	5.447	4.392
		1125-1205	427.9	51.4	47.6	33.7	5.711	5.288	3.751
	6/17/93	1100-1145	427.9	44.0	44.8	34.3	4.892	4.979	3.811
Lay-Up #3	6/16/93	1030-1110	404.2	29.7	28.6	26.0	3.116	3.003	2.727
		1125-1205	404.2	31.3	30.2	37.6	3.285	3.175	3.946
Back-Up #1	6/16/93	1245-1330	370.1	100.7	N/A	92.8	9.680	N/A	8.925
		1245-1330	370.1	105.1	N/A	92.3	10.100	N/A	8.873
	6/17/93	0825-0910	378.4	68.3	N/A	45.4	6.711	N/A	4.462
		0825-0910	378.4	74.3	76.0	40.2	7.305	7.472	3.949
EMISSIONS FOR VENTS OR BOOTHS WHERE NO STYRENE WAS SPRAYED									
Exhaust 1	6/21/93	0812-0830	363.5	8.0	N/A	N/A	0.758	N/A	N/A
Exhaust 2	6/21/93	0840-0913	163.1	9.7	N/A	N/A	0.412	N/A	N/A
Exhaust 3	6/21/93	0916-0940	331.4	9.6	N/A	N/A	0.823	N/A	N/A
Resin Mix	6/21/93	1326-1340	187.9	7.2	N/A	N/A	0.352	N/A	N/A
Lay-Up #4	6/21/93	1154-1229	396.9	8.7	N/A	N/A	0.894	N/A	N/A
Lay-Up #5	6/21/93	1302-1315	379.1	10.2	N/A	N/A	1.005	N/A	N/A
Lay-Up #6	6/21/93	1250-1300	353.5	13.9	N/A	N/A	1.273	N/A	N/A
Back-Up #2	6/21/93	1316-1324	367.3	8.2	N/A	N/A	0.779	N/A	N/A
Total (All Vents) = 6.295									
AVERAGE EMISSIONS PER BOOTH DURING MORNING AND LUNCH BREAKS (NO SPRAYING ACTIVITY)									
Gel Coat #1	6/15/93	1003-1024	374.3	6.9	N/A	N/A	0.674	N/A	N/A
Gel Coat #2	6/15/93	1003-1024	373.6	9.9	N/A	N/A	0.961	N/A	N/A
Gel Coat #2	6/22/93	1005-1031	373.6	N/A	7.5	N/A	0.732	N/A	N/A
Back-Up #1	6/17/93	1000-1030	370.1	5.2	N/A	N/A	0.498	N/A	N/A
Lay-Up #1	6/16/93	1207-1224	358.8	7.0	N/A	N/A	0.653	N/A	N/A
Average (per booth) = 7.0 Average (per booth) = 0.668									

Table 5. Styrene Emissions per Unit Area of Mold Sprayed, Eljer Plumbingware (June 1993)

Sampling Location	Date	Sampling Time Span	Sample Time (min)	Mold Area (m ²)	Vent Flow Rate (dscmm)	----Styrene Emitted----	
						THC (g/m ²)	Method 18 (g/m ²)
Gel Coat #1	6/15/93	0900-0945	45	44.50	374.3	74.4	35.3
		1030-1115	45	43.66	374.3	99.4	55.7
		1120-1205	45	36.14	374.3	120.5	79.1
	6/17/93	1245-1330	45	0.00	374.3	N/A	N/A
Gel Coat #2	6/15/93	0900-0945	45	38.55	373.6	114.2	46.7
		1030-1115	45	N/A	373.6	N/A	N/A
		1120-1205	45	N/A	373.6	N/A	N/A
	6/17/93	1245-1330	45	54.63	373.6	90.2	49.1†
Gel Coat #3	6/16/93	0740-0825	45	34.19	362.2	125.7	81.9
		0830-0915	45	22.30	362.2	111.6	86.4
		0920-1005	45	23.97	362.2	148.0	121.9
	Gel Coat Booth Average =						110.5
Relative Standard Deviation (%) =						20.5	40.6
Lay-Up #1	6/16/93	0740-0825	45	28.43	358.8	126.4	68.3
		0830-0915	45	30.10	358.8	115.1	70.6
		0920-1005	45	27.22	358.8	130.7	90.6
	6/17/93	1100-1145	45	34.19	358.8	78.9	60.8†
Lay-Up #2	6/16/93	1030-1110	40	22.99	427.9	162.1	127.3
		1125-1205	40	19.51	427.9	187.9	128.2
	6/17/93	1100-1145	45	N/A	427.9	N/A	N/A
Lay-Up #3	6/16/93	1030-1110	40	40.13	404.2	50.8	45.3
		1125-1205	40	28.24	404.2	76.3	93.1
Lay-Up Booth Average =						116.0	85.5
Relative Standard Deviation (%) =						39.7	35.3
Back-Up #1	6/16/93	1245-1330	45	103.58	370.1	70.1	64.6
		1245-1330	45	103.58	370.1	73.1	64.3
	6/17/93	0825-0910	45	80.27	378.4	62.7	41.7
		0825-0910	45	80.27	378.4	69.0	36.9
Back-Up Booth Average =						68.7	51.9
Relative Standard Deviation (%) =						6.4	28.2

* Video camera failure.

** Video Camera pointed at wrong booth, no data.

† Value may be in error due to shift in GC calibration during analysis.

Table 6. Determination of Non-Spray Booth Styrene Emission Rate

Activity	Amount	Unit
All Vents During Spraying [*] =	37.773	kg/day
All Vents During Breaks ^{**} =	9.443	kg/day
Usually Active Spray Booths During Breaks [†] =	7.012	kg/day
All Vents, All Day, (THC measurements only) =	54.227	kg/day

* Active spray booths excluded, (6 h of ventilation/day) x (6.295 kg/h from non-spraying vents).

** Active spray booths excluded, (1.5 h of breaks/day) x (6.295 kg/h from non-spraying vents).

† Booths normally used for spraying, (1.5 h of breaks/day) x (0.668 kg/h per booth during breaks) x (7 booths).

Table 7. Plant Raw Material and Styrene Usage, June 15-17, 1993

Date	-----Mass of Material Used-----			----Amount Sprayed----		----Styrene Emitted----	
	Gel Coat (kg)	Lay Up (kg)	Back Up (kg)	Total [*] (kg)	Styrene ^{**} (kg)	THC (kg)	Method 18 (kg)
6/15/93	488.1	2237.1	1947.3	4672.4	1042.9	246.0	188.4
6/16/93	516.2	2124.6	1811.6	4452.4	999.5	244.2	187.4
6/17/93	513.0	2155.9	1798.9	4467.9	1002.5	246.9	189.2
Total	1517.3	6517.6	5557.8	13592.7	3044.9	737.1	565.0

Date	-----Area Sprayed-----			-----Areal Density-----		
	Gel Coat [†] (m ²)	Lay Up (m ²)	Back Up (m ²)	Gel Coat (kg/m ²)	Lay Up (kg/m ²)	Back Up (kg/m ²)
6/15/93	664.6	640.5	640.5	0.7344	3.4930	3.0404
6/16/93	646.0	642.0	642.0	0.7990	3.3092	2.8217
6/17/93	653.0	652.1	652.1	0.7856	3.3063	2.7588
Total	1963.6	1934.5	1934.5	0.7727	3.3691	2.8729

* Not counting MEKP. See Table 3 for details of raw material use.

** Gel Coat = 32.2% styrene, Lay-Up Mix = 21.4% styrene, Back-Up Mix = 20.9% styrene.

† Includes molds rejected due to imperfections.

Table 8. Styrene Emissions for Each Part of the Manufacturing Process

(a) Styrene Emissions per Unit Area of Mold Sprayed

Emissions from:	----- THC Analyzer -----		----- EPA Method 18 -----	
	Styrene	Pop. Std. Dev.	Styrene	Pop. Std. Dev.
	(g/m ²)	(g/m ²)	(g/m ²)	(g/m ²)
Gel Coat Booths	110.5	21.2	69.5	26.4
Lay Up Booths	116.0	43.1	85.5	28.3
Back Up Booths	68.7	3.8	51.9	12.6
Non-Spray Booth Emissions	83.7	N/A	83.7	N/A
All Emissions	378.9	48.1*	290.6	40.7*

(b) Percent of Total Mass Used in Each Stage of Manufacture that was Emitted as Styrene

Emissions from:	----- THC Analyzer -----		----- EPA Method 18 -----	
	Styrene	Rel. Std. Dev.	Styrene	Rel. Std. Dev.
	(%)	(%)	(%)	(%)
Gel Coat Booths	14.3	2.7	9.0	3.4
Lay Up Booths	3.4	1.3	2.5	0.8
Back Up Booths	2.4	1.5	1.8	0.4
Non-Spray Booth Emissions	1.2	N/A	1.2	N/A
All Emissions	5.4	0.7*	4.2	0.6*

(c) Percent of Styrene Used in each Stage of Manufacture that was Emitted

Emissions from:	----- THC Analyzer -----		----- EPA Method 18 -----	
	Styrene	Rel. Std. Dev.	Styrene	Rel. Std. Dev.
	(%)	(%)	(%)	(%)
Gel Coat Booths	44.4	8.5	27.9	10.6
Lay Up Booths	16.1	6.0	11.9	3.9
Back Up Booths	11.4	0.6	8.6	2.1
Non-Spray Booth Emissions	5.3	N/A	5.3	N/A
All Emissions	24.2	3.3*	18.6	2.8*

* Minimum estimate. Assumes each process independent with no contribution from the non-spraying emissions component.

18 procedure, styrene can polymerize before analysis and may also have a very low vapor pressure at stack or instrument conditions. Both of these conditions would result in a lower measurement for styrene.

Although it is not specifically noted in AP-42,¹ it is reasonable to assume that styrene emission factors cited in this standard for polyester resin plastics products fabrication include emissions not captured by active spray booths. Thus, in order to compare the results obtained in this study with those cited in AP-42, it is necessary to apportion styrene emissions from non-spray booth emissions to those parts of the process associated with spraying operations: gel coating, lay-up and back-up. The following approach was followed to apportion non-spray booth emissions to each of the spraying operations.

1. Obtain an average emission factor for each of the spraying operations by averaging the Method 18 and THC measurements for each of the three spraying operations (gel coating, lay-up and back-up)
2. Apportion emissions not directly associated with spraying to each of the three spraying operations as follows:
 - 2.1 Assume that vents that are in the close proximity to a particular spraying operation capture the emissions (from curing molds) generated by that operation. Some non-spraying emissions are surely captured by active spray booths. However, for the purposes of apportioning emissions to obtain a comparison with AP-42, we will assume that all emissions captured by an active spray booth are emissions directly related to that phase of manufacture.
 - 2.2 Thus, because the area of the plant used for gel coating is more or less off by itself, we assume that the three exhaust fans on the side of the plant adjacent to the gel coat spray booths capture curing emissions from molds previously sprayed in one of the three gel coat booths. Likewise, we will assume that lay-up booths 4, 5, and 6, (that were not used for spraying) capture styrene emissions from molds that were sprayed in lay-up booths 1, 2,

and 3, and we will assume that back-up booth 2 (that was not used for spraying) captures styrene emissions from molds that were sprayed in back up booth 1.

2.3 Similarly, we will assume that during breaks in spraying (morning break, lunch) any emissions captured by a particular spray booth came from molds that were sprayed in the phase of manufacture normally associated with that spray booth. This includes styrene emissions captured during the 15 minutes before work commenced, the 30 minute midmorning break, the 30 minute lunch break, and the 15 minutes that the vents are operated at the end of the day after spraying has ended.

2.4 Assume that resin mixing room emissions that are exhausted to the atmosphere can be apportioned to emissions from the lay-up and back-up operations because these resins are only used in those phases of manufacture; gel coat is supplied in pre-mixed 55 gallon drums. We will apportion the resin mixing room emissions according to the mass of mix sprayed in each of the two operations.

Using these assumptions, the following emission factors were calculated:

Gel Coat	47.5% of the styrene sprayed in that phase of manufacture
Lay-Up	20.0% of the styrene sprayed in that phase of manufacture
Back-Up	12.1% of the styrene sprayed in that phase of manufacture

These data suggest that spray booth emissions are higher than those cited in AP-42 for gel coating and spray lay-up (see Table 1, reproduced from AP-42, for styrene emission factors).¹ AP-42 cites a value of from 26 to 35% of styrene monomer being emitted for gel coat that contains no vapor suppressing additives (as was the case at Eljer). The results calculated according to the above procedure to apportion non-spraying emissions to each part of the manufacturing process that incorporates spraying suggest that nearly 48% of the styrene in the gel coat mix is lost to the atmosphere.

AP-42 makes no distinction between styrene emissions from lay-up booths or from back-up booths, and indicates that, with vapor suppressing additives in the mix, from 3 to 9% of the styrene sprayed in this operation is emitted. If vapor-suppressing additives are not added to the mix, emissions rise to from 9 to 13% of the styrene sprayed. At Eljer, vapor suppressants are added to the lay-up and back-up mix. However, the levels of styrene emissions measured there suggest that the emissions levels are probably higher than what AP-42 cites as typical for non-vapor suppressed emissions, particularly for the lay-up phase of manufacture. Thus, results calculated according to the above apportioning procedure show that styrene emissions to the atmosphere averaged 20% of the styrene sprayed in the lay-up booths and 12% of the styrene sprayed in the single back-up booth.

These generally higher than expected emission levels may be, at least in part, due to the nature of the process. At the Eljer facility (which is probably like other such manufacturing plants), molds that have been sprayed are frequently left near the mouths of spray booths where spraying is in progress. Hence, styrene evolved from a curing mold can be captured by an adjacent spray booth. While this practice is not common in the gel coat booths (because of limited space in front of the booths at the Eljer facility); this practice is an integral part of the manufacturing process for the latter two stages of spraying. In fact, at any one time, it is common for as many fifteen molds to be in various stages of manufacture in the general vicinity of the lay-up and back-up booths. Also, molds are generally left in a lay-up booth between sprayings where the surface of the mold is rolled flat. In AP-42 it is noted that styrene emissions are increased by such manual rolling.¹

Finally, AP-42 provides no separate estimate of styrene emissions not captured by spray booths. While such emissions are certainly a function of ventilation system design and the specific equipment at a given facility, at Eljer it was found that 6% of *all* the styrene sprayed exits the facility through openings other than spray booth exhausts. As noted in Table 9, this corresponds to from 22 to 29% (depending on the measurement method) of all styrene emitted to the atmosphere; thus, styrene emissions not captured by spray booths represent a source of styrene emissions as great as (or possibly greater than) styrene emissions associated with any one of the spraying operations.

Table 9. Distribution of Styrene Emissions from Each Part of the Manufacturing Process, Including Styrene Emissions not Captured by Spray Booths

Date	----- From THC Analyzer Measurements -----					----- From Method 18 Measurements -----				
	Gel Coat Booths (%)	Lay Up Booths (%)	Back Up Booths (%)	Non-Spraying (%)	All Source s (%)	Gel Coat Booths (%)	Lay Up Booth s (%)	Back Up Booths (%)	Non-Spraying (%)	All Source s (%)
6/15/93	29.9	30.2	17.9	22.0	100.0	24.5	29.1	17.6	28.8	100.0
6/16/93	29.2	30.5	18.1	22.2	100.0	24.0	29.3	17.8	28.9	100.0
6/17/93	29.2	30.6	18.2	22.0	100.0	24.0	29.5	17.9	28.6	100.0
Average	29.4	30.5	18.0	22.1	100.0	24.2	29.3	17.7	28.8	100.0

RECOMMENDATIONS FOR FUTURE SAMPLING

Three methods are available to measure hydrocarbon emission rates for an emission source such as Eljer Plumbingware. Two of the three methods were used here: EPA Method 18 (using Tedlar bags to obtain time-averaged samples) and THC analyzers (direct sampling through heated hoses). The third method that is appropriate is a variation of Method 18 that uses a charcoal-filled adsorption tube instead of a Tedlar bag to obtain a time integrated aerosol sample. With this method, styrene (or another VOC) that was adsorbed on the activated charcoal during sampling is desorbed in a known volume of carbon disulfide (usually in the laboratory). Then, a known volume of the carbon disulfide and desorbed hydrocarbon mixture is injected directly into a GC, usually equipped with an FID.

The advantage of the first two methods is that results are obtained on site and while the Method 18 procedure using Tedlar bags is complex, it has been used successfully for some time and is well documented.⁵ THC analyzers have also been used for a number of years and usually employ an FID for detection. With these devices, time averaging is accomplished by averaging recorded instrument response over the period of interest. Important caveats for THC analysis are that first, if more than one hydrocarbon is

present, some way must be found to determine the relative concentration of each component (presuming the split remains constant throughout the sampling period) and second, the instrument should be calibrated with the compound that is being measured (at a concentration near that which is expected, if possible). An on site GC-FID could be used for speciation (from direct sampling) or samples obtained with adsorption tubes (taken concurrently with other measurements) could be used to provide compound speciation.

The problems encountered in this investigation were exacerbated by inaccurate styrene concentration determinations on the part of Matheson Gas Products for the calibration gas standards. However, the general disagreement between the THC analyzers and the EPA Method 18 Tedlar bag results cannot be due to inaccurate calibration gases because both instruments were calibrated with the same calibration gas standards. Thus, though absolute response in the field was in error, this problem was eliminated when the data were corrected according to the procedures documented in Appendix A. This disagreement does suggest that it would have been desirable to use a third method to ascertain which of the two other methods were in error. Some EPA Method 18 adsorption tubes should have been run during the test (concurrent with other sampling) to provide a third, separate determination of styrene concentration. In the future, such a procedure should be followed. Thus, in a future emissions test, two techniques (perhaps Method 18 with Tedlar bags and THC analyzers) should be used to measure hydrocarbon concentration and, at a minimum, some Method 18 adsorption tubes should be taken concurrently with other samples. In the case of a disagreement, results from the analysis of the adsorption tubes could be used to determine which technique provides the best results. In the case where time is available, Method 18 samples with adsorption tubes could be taken on the first day of sampling and be analyzed immediately so that the results from the adsorption tube analysis could be compared with results from the other two methods.

Two final recommendations are in order. First, all calibration standards should be independently checked before a field evaluation commences. Second, it is also recommended that prior to any emissions testing, an EPA audit standard should be obtained and evaluated to validate laboratory standard operating procedures.

SECTION 5

REFERENCES

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APPENDIX A

QUALITY CONTROL EVALUATION REPORT

SUMMARY

A Quality Assurance Project Plan (QAPP) was written and approved for this project. No field audits were planned or performed. However, as stated in the QAPP, vendor-certified calibration gases (3, 52, 54, and 195 ppmv of styrene in nitrogen and zero air with less than 0.1 ppm THC content) served as field performance audit samples for EPA Method 18 and THC sampling. Unfortunately, as documented below, the concentrations of the styrene calibration gases were incorrectly determined by the vendor, Matheson Gas Products. Actual concentrations were determined to be 2.2, 39.1, 39.4, and 170.8 ppmv of styrene, respectively. EPA personnel were on site to oversee diagnostic measurements. In the field, QC was addressed by adherence to standard sampling protocols either as specified for EPA Method 18 or by following a standard operating procedure (modified as needed for this particular sampling task) with the THC analyzers as specified in the THC instruction manual.

In the Southern Research Analytical Chemistry facilities, QC is addressed by strict adherence to standard operating procedures (SOP) previously defined and implemented. While random audits can occur while the field samples from any project are being analyzed, and audits are regularly performed by the QA officer at this facility, no audit was planned or performed as part of this project.

Overall, the data quality indicator (DQI) goals were not achieved. This is partially due to reduced plant availability because the work week at the plant was one day less than was expected when the project was initiated. Mainly, the DQI goals were not achieved because significant problems were encountered with

the calibration gases purchased for this test. These difficulties are discussed in detail in the following section on QA/QC problems.

With respect to plant availability, we were able to perform Method 18 sampling for only three of the four days that were originally planned. Unfortunately, because the following week was scheduled for a second phase of this Work Assignment, the testing of a liquid chemical scrubber, only a minimal extension of this testing could be accommodated. Within these constraints the Project Officer concluded that in order to obtain the needed data within the time available Method 18 sampling would focus on the operational spray booths (a total of seven) while styrene emissions not captured by active spray booths (spray booths used as ventilation air exhausts and separate ventilation air fan exhausts) would be measured with the THC analyzers. Thus, from June 15 through 17, Method 18 testing was conducted at the spray booth exits and the THC analyzers were used as continuous monitors to measure styrene emissions at the same locations and times used for Method 18 sampling. On Monday, June 21, while preparations were underway to begin Phase 2 of this Work Assignment, the THC analyzers were used to quantify styrene emissions not captured by active spray booths that had not been determined during the previous week of testing.

SIGNIFICANT QA/QC PROBLEMS

One significant QA/QC problem was encountered. After sampling for both phases of the Work Assignment had been completed, samples of the nominal 3 and 52 ppmv styrene cylinder gas standards taken in the field on June 24 with Method 18 (Section 7.4, Absorption Tube Procedure, equivalent to NIOSH Method 1501) were analyzed to verify sample recovery for the second phase of this Work Assignment. These samples were analyzed on July 7. Styrene concentrations of 2.3 and 35.8 ppmv were determined corresponding to vendor-certified values of 3 and 52 ppmv. Such large discrepancies between the styrene concentrations certified by Matheson Gas Products and the styrene concentrations measured with the adsorption tubes suggested that the vendor-certified concentrations of these calibration gases were in error or that some part of the laboratory analysis performed by Southern was incorrect. Therefore, a two-pronged

investigation followed that focused on the possibility that the styrene calibration gases were in error, that Southern made incorrect determinations of the styrene content in the calibration gases, or a combination of the two possibilities occurred.

With respect to the calibration gases, two bottles each of the low styrene concentration (nominal 5 ppmv styrene in nitrogen) and intermediate styrene concentration (nominal 50 ppmv styrene in nitrogen) calibration gases were ordered from Matheson Gas Products for this test on May 13, 1993 and were received in early June. As indicated above, Matheson Gas Products certified that the styrene content in the two bottles of low concentration gas were actually 3 ppmv while the styrene concentration in one of the intermediate calibration standards was 52 ppmv and the other intermediate concentration standard was 54 ppmv. Two cylinders of the high calibration standard (nominal 200 ppmv styrene in nitrogen) were ordered on September 30, 1992 for an earlier EPA-sponsored test at the Eljer facility. These gases were received in mid-October, 1992. One cylinder of this gas was not used during that test and was taken on this test for use as a high styrene concentration calibration gas. Matheson certified that the styrene content was 195 ppmv for this cylinder. Matheson Gas Products was contacted and a representative indicated that as far as their records indicated, the cylinders were properly prepared and passivated and that stable styrene concentrations were determined in their laboratory (and were recorded on the calibration tags supplied with each cylinder) when the gases were shipped to Southern.

With respect to Southern's laboratory procedures, while conversations were being held with Matheson Gas Products, two other samples of the 3 and 52 ppmv styrene calibration gases were taken on July 13 and analyzed to check the procedures followed during the earlier analyses. In addition, different high-purity liquid laboratory standards for styrene (from two different suppliers, Aldrich and Chem Service) were used to prepare independent calibration standards that were checked against one another on the same GC FID used for both sets of analyses. Approximately six calibration standards (of different concentrations below, centered about, and above those measured from the earlier analyses of the adsorption tubes) were prepared by adding a known quantity of each high-purity liquid styrene standard to a known quantity of high-purity carbon disulfide. Known microliter volumes of these liquid mixtures were then injected into the GC-FID

used for the adsorption tube analyses and the peak areas were recorded and averaged. No statistically different result was determined for the two liquid styrene standards and the analyses of these two adsorption tube samples were consistent with the earlier results. To make a definitive assessment of the actual styrene content of the Matheson-certified 3 and 52 ppmv styrene calibration gases, on July 29 and 30, four adsorption tube samples each were taken from each calibration gas cylinder (using Method 18, the adsorption tube procedure). Two adsorption tube samples of each styrene calibration standard were taken inside (at an average laboratory temperature of 22°C) and two adsorption tube samples were taken outside with the calibration gas bottles in the direct sun (an average temperature of 38°C). The reason samples were taken at laboratory conditions and at conditions that mimicked ambient field temperatures experienced at the Eljer facility was to determine if styrene gas was condensed within the sampling apparatus at room temperature - a possible explanation for the apparent low recovery based on Matheson's certified values. The adsorption tubes (from the same lot used at Eljer: SKC, Inc. catalog # 226-01, coconut charcoal, Lot 120) were analyzed by removing the charcoal from the tubes and desorbing the styrene into high-purity carbon disulfide. As part of the analytical procedure, the desorption efficiency of styrene from this lot of coconut charcoal is separately determined each time a sample or set of samples is analyzed. The desorption efficiency was determined to be 90.25%, equal to the value that has been determined in the past. The results of these analyses, carried out during the first week of August, was that no difference could be detected between samples obtained inside or outside the laboratory and that the Matheson-certified 3 ppmv styrene gas was 2.69 ppmv with an RSD of 3.55% while the Matheson-certified 52 ppmv styrene gas was 39.1 ppmv with an RSD of 0.55%. No error was found in the analytical procedures followed in these analyses, in the preparation of the two sets of calibration standards, or in the behavior or operation of the GC-FID used for these analyses.

Next, a performance evaluation audit standard was requested from EPA to determine with certainty if the error was due to our analytical procedures. The cylinder was sent to Southern on September 17 and the results of Southern's triplicate analysis (using the Method 18, Adsorption Tube Procedure) of the styrene content in the cylinder was reported to the EPA on September 21. After it was determined that Southern's

analysis was within 96.6% of the actual styrene concentration of 58.6 ppmv (with an accuracy of $\pm 2.2\%$), it was concluded that the concentrations reported on Matheson's analysis of all the gas samples provided for this test were in error. The results of the tests of the EPA performance evaluation audit sample are shown in Table A-1. Table A-2 shows the results of tests performed to determine the actual styrene content of these gases. No other corrective actions were required or taken during the collection of samples and data or during subsequent analysis of samples collected during testing.

The values reported in Table A-2 were obtained by two separate methods. First, as part of the investigation discussed above, EPA Method 18, Adsorption Tube Procedure (equivalent to NIOSH Method 1501), was used to make triplicate determinations of the styrene content of each of the nominal 3, 52, 54, and 195 ppm styrene calibration gases. All of these determinations were completed by September 14. Second, on September 29, a JUM VE-7 THC analyzer (one of the THC analyzers used in the sampling van) was allowed to stabilize for 24 hours on filtered ambient laboratory air and was then spanned with 10.7 ppm $\pm 1\%$ propane (unfortunately, other propane standards were not available when these measurements were performed) and zeroed with a THC-free zero air standard (≤ 0.1 ppm of hydrocarbon compounds). The THC analyzer was then used to sample the 58.6 ppm EPA audit standard, as well as the nominal 3, 54, and 195 ppm styrene calibration gases (at this time the cylinder containing the 52 ppm calibration gas had been exhausted). Styrene content was determined based on the response of each of the calibration gases to the value measured for the EPA audit standard. Zero and span checks performed at the beginning, middle and at the end of the THC measurements confirmed instrumental stability.

These results required that, at best, all of the data be scaled to reflect the true concentrations of styrene present in the gas cylinders obtained from Matheson Gas Products that were used for field calibrations. At worst, the data could be completely compromised because the styrene within the cylinders supplied by Matheson could have been slowly polymerizing since the cylinders were prepared and the styrene concentrations measured after the test would *not* represent styrene concentrations

Table A-1. Results of Analyses of EPA Performance Evaluation Audit Sample*

Sample**	Measured (ppm)	Actual (ppm)	Rel % Difference
1.	55.6	58.6	-5.1
2.	57.0	58.6	-2.7
3.	57.1	58.6	-2.6
Average \pm RSD	56.6 \pm 1.5%	58.6 \pm 2.2%	-3.4

* Cylinder CLM 008308. Specified as containing styrene at a concentration under 100 ppm with the balance gas being nitrogen. Content later quoted by EPA to be 58.6 ppm \pm 2.2% RSD.

** Analysis by EPA Method 18, Absorption Tube Procedure, with GC/FID. Aside from the diluent (CS₂), styrene was the only material detected.

Table A-2. Results of Analyses of Matheson Calibration Gas

Matheson Analysis (ppm)	Method 18 Analysis** (ppm)	RSD (%)	THC Analysis† (ppm)	RSD (%)	Comparability (% Diff.)
3	2.69	3.55	2.16	0.25	21.9
52	39.1	0.55	N/A††	--	--
54	37.8	2.07	39.45	0.12	-4.3
195	176.8	4.06	170.8	0.18	3.5

* As indicated on gas cylinder, ppm styrene in nitrogen.

** Absorption Tube Procedure using charcoal tubes.

† THC calibrated with 10.7 ppm propane in nitrogen. Response referred to styrene by analysis of EPA performance evaluation audit sample (58.6 ppm styrene measured 151.06 \pm 0.24 ppm with propane-based calibration).

†† Cylinder exhausted before THC measurements could be made.

present in the cylinders at the time of the test. The latter eventuality was explored with Matheson in the initial conversations that were directed toward determining the source of the disagreement. As indicated above, Matheson Gas Products asserted that the cylinders were properly prepared and passivated. While Matheson was unable to explain why the concentrations were so far from those determined by their original in-house analysis, they did maintain that if the temperature indicating strips on the sides of the cylinders had

not changed color (indicating exposure to temperatures that could degrade the sample), styrene concentrations within the cylinders should have remained stable through the time period of the test and our subsequent determination of the actual styrene concentrations within the cylinders. Because none of the temperature indicating strips on the sides of the cylinders had changed color (indicating the temperature of the cylinder had reached or exceeded 125°F), we proceeded to correct the data assuming that styrene concentrations in the calibration cylinders measured after the test were representative of styrene concentrations present during testing.

Both THC data and EPA Method 18 data required correction. Correction of the THC data was relatively straightforward. Lab THC data was taken on THC analyzers calibrated with propane (850 ppm, \pm 1%). During the test, the nominal 54 ppm styrene calibration gas (actually 39.45 ppm by later THC analysis) was observed to produce an equivalent propane response of 115 ppm on THC#1 and 116 ppm on THC #2. Thus, these data were scaled by the ratio of 0.3430 (or 39.45/115) for THC #1 and 0.3401 (or 39.45/116) for THC #2. Both THC analyzers in the sampling van were calibrated with the same nominal 52 ppm styrene calibration gas (actually 39.1 ppm by Method 18 analysis). Because this cylinder was emptied before the THC measurements reported in Table A-2 could be made, results obtained with these analyzers were scaled by a ratio of 0.7519 (or 39.1/52).

The EPA Method 18 data required more extensive correction. The concentration of a VOC as measured by a gas chromatograph is determined by first measuring the instrumental response (peak area) to a set of calibration gases and then relating the peak area measured for each calibration gas to the known concentration of that gas. Because a FID produces a linear response to concentration, a linear fit is usually made to the peak area (x) versus concentration calibration (y) data.

In the field, after measuring the peak area response to each calibration gas (nominal 3, 54, and 195 ppm styrene), linear fits were made to relate peak area to styrene content for subsequent determinations. Thus, to correct the GC data obtained on this test, each linear (calibration) fit obtained in the field was recalculated based on what the actual styrene concentration of each calibration gas was later determined to be and the styrene concentrations obtained during the time that calibration was used were corrected with the new linear fits. For these corrections, the THC analyzer-determined values for the calibration gases were

used because during those measurements repeated, direct comparisons were made with the EPA audit standard. Table A-3 presents the calibration data determined for each day of testing (on site).

Table A-3. GC-FID Calibrations Performed at Eljer Plumbingware*

Nominal Styrene Concentration (ppm)	Actual Styrene Concentration (ppm)	GC-FID Peak Area 6/15/93 (0935-1151)	GC-FID Peak Area 6/16/93 (0819-0902)	GC-FID Peak Area 6/17/93 (1052-1145)	GC-FID Peak Area 6/21/93 (before 0800)
3	2.16	4994	3903	6986	9428
54	39.45	118910	100744	273351**	201447
195	170.8	343248	364290	968576	780310

* Performed by DEECO, Inc..

** Reanalysis at 1346 gave peak area of 176150

During the test, full instrumental calibrations were performed early each morning and afterwards, occasional checks were performed with the nominal 54 ppm calibration standard to assure that instrument response had not drifted. Because of the limited time available for sampling (due to the plant operating schedule) only one full calibration was performed each day.

These corrections are not completely satisfactory. In particular, the peak area measured for the 195 ppm styrene calibration gas (actually 170.8 ppm by subsequent THC analysis), appears to be low as compared to the other two calibration gases. It could be that this relatively high concentration of styrene did change between the time the test was performed and the time that the concentration of this calibration gas was measured in the laboratory. Another likely possibility is that the Teflon sampling line that was used to convey this gas to the GC was not kept warm enough (the lab trailer was air conditioned and maintained at approximately 75°F) and some of the styrene condensed in the line before it could reach the inlet of the GC. Before the test this concentration of styrene had been observed to condense in Teflon sampling lines under similar laboratory conditions. Because of this discrepancy, and because few of the styrene concentrations measured were greater than 100 ppm (corrected), it was decided to eliminate the 195 ppm (actual 170.8 ppm) point from the set of calibration data from which new fits were determined to correct the original data.

One other significant problem was encountered in correcting the GC data. On June 17, at the morning calibration, GC response to styrene was observed to have increased dramatically as compared to the response measured during earlier calibrations. Afterwards, instrumental response was monitored closely while two samples (one from a Tedlar bag and another from a Teflon bag) were repeatedly analyzed. Approximately one hour after that calibration, the GC was observed to have stabilized at a lower response level and a single point calibration was performed with the 54 ppm (39.45 ppm actual) so that samples that had been accumulating could be analyzed. Thus, we were forced to rely on a single point calibration for Method 18 data acquired on June 17.

DATA QUALITY

The following procedures were used to determine how well data DQI goals were met:

- Precision is expressed as percent coefficient of variation:

$$\% CV = 100 \times (S_x/X_{avg})$$

where S_x is the standard deviation of x number of data values from the data set and X_{avg} is the mean or average of the x number of data values from the data set.

- Bias is expressed as a difference or percent difference between measured and known values:

$$\text{Bias} = (X - T)$$

$$\%RPD = 100 [(X - T)/T]$$

where T is the true value (reference standard) and X is the mean sample concentration. %RPD is the relative percent difference.

- Completeness is expressed as a percent between successful analyses and total attempts:

$$\text{Completeness} = 100 \text{ S/A}$$

where S is the number of successful analyses and A is the total number of attempts.

- Comparability is expressed as a percent difference (%Diff) between the results for two methods:

$$\%Diff = 100 (R_1 - R_2) / [(R_1 + R_2)/2]$$

where R_1 is the result for one method and R_2 is the result for the second method.

Table A-4 shows the DQI goals that were estimated for critical measurements in the QAPP, and Table A-5 presents the DQI values for measurements carried out with EPA Reference Method 18 and the THC analyzers in the sampling van and the mobile lab. Below, the precision, accuracy, and completeness of the data that were obtained in this project are reviewed.

Precision

Precision, as reported in Table A-5 (a), meets the DQI goals shown in Table A-4 for Method 18 with the exception of the 170.8 ppm calibration point which was expected. Mainly, this is because field calibrations were compromised by incorrect concentrations for the calibration gases. Using the procedure described above, the values reported in Table A-4 (a) were obtained by generating new fits to the original calibration data (excluding the 170.8 ppm point), as taken for each day of testing and then determining the difference between the correct styrene concentration (from THC remeasurement) and styrene concentrations determined from best linear fit to the calibration data.

Table A-4. Data Quality Indicator Goals for Critical Measurements Estimated in QAPP

Method and Reference	Measurement Parameter	Experimental Condition	Expected Precision (RSD, %)	Expected Accuracy (% Bias)	Completeness (%)
EPA Method 18, Section 7.1 and Section 7.3	VOC Speciation and Concentration	1. Spray booth. Vent and air exhausts. 2. Headspace measurements from styrene storage tanks.**	5.0*	10*	90
Total Hydrocarbon Analyzer with FID†.	Hydrocarbon compounds in air.	1. Spray booth Vent and air exhausts. 2. Headspace measurements from styrene storage tanks.**	± 10††	± 5††	90

* Expected precision and bias for GC-FID analysis of samples obtained using EPA Method 18. Precision and bias will be determined for the GC-FID used (Shimadzu GC-14A).

** Headspace measurements eliminated from testing by Project Officer.

† J.U.M. Model VE-7 THC Analyzer with FID.

†† Estimated values.

Table A-5. Data Quality Indicator Values for Method 18 and THC Measurements Made at Eljer Plumbingware

(a) Method 18 Measurements in Mobile Lab

Cal Gas, % Bias	2.16 ppm Styrene Cal Gas (Method 18 Value)	Bias %	39.4 ppm Styrene Cal Gas (Method 18 Value)	Bias %	170.8 ppm Styrene Cal Gas (Method 18 Value)	Bias %
6/15/93	2.23	3.2	39.4	0	112.6	-34
6/16/93	2.23	3.2	39.4	0	140.5	-18
6/17/93	2.19	1.4	39.4	0	136.5	-20
6/21/93	2.20	1.9	39.4	0	152.6	-11
Average	2.21	2.4	39.4	0	135.3	-21
Precision (% CV)	0.9		0.0		12.1	

(b) THC Measurements Made in Sampling Van, THC #1 and THC #2

THC #1 Cal Gas/% Bias	2.16 ppm Styrene Cal Gas (THC Value)	Bias %	170.8 ppm Styrene Cal Gas (THC Value)	Bias %
6/15/93	3.03	40	178.2	4
6/16/93	2.69	25		
6/17/93	2.51	16		
Average	2.7	27	--	--
Precision (% CV)	9.6		--	
THC #2 Cal Gas/% Bias	2.16 ppm Styrene Cal Gas (THC Value)	Bias %	170.8 ppm Styrene Cal Gas (THC Value)	Bias %
6/15/93	2.82	31	174.9	2
6/16/93	2.60	20		
6/17/93	2.58	19		
Average	2.67	24	--	--
Precision (% CV)	5.0		--	

(c) THC Measurements Made in Mobile Lab, THC #1 and THC #2

Date	THC #1 850 ppm Propane Cal Gas	Bias %	THC #2 850 ppm Propane Cal Gas	Bias %
6/15/93	848	-0.2	860	1.2
	856	0.7	856	0.7
			860	1.2
6/16/93	851	0.1	856	0.7
	850	0.0	856	0.7
			848	-0.2
6/17/93	859	1.1	848	-0.2
6/21/93	850	0.00	840	-1.2
Average	852	0.3	853	0.4
Precision (% CV)	0.5		0.8	

As with the Method 18 measurements, for the THC analyzers in the sampling van precision was determined by repetitive sampling of calibration gases. Because of suspected problems with line losses the 170.8 ppm calibration gas was only sampled once. Precision was determined by repetitive sampling of the 2.16 ppm styrene calibration gas. The results of these determinations, shown in Table A-5(b), are within the DQI goals shown in Table A-5.

With respect to the determination of precision for the THC analyzers in the mobile laboratory, these analyzers were calibrated with 850 ppm propane. Precision was determined by repetitive sampling of the 850 ppm propane calibration gas. The results of these determinations, shown in Table A-5(c), are well within the DQI goals shown in Table A-4. The relative response of each THC to styrene was determined on June 17. After both analyzers had been calibrated with the propane standard, nominal 54 ppm (actual 39.45 ppm) styrene calibration gas was fed to both THC analyzers. THC #1 read 115 ppm and THC #2 indicated 116 ppm.

Bias

For Method 18 measurements, bias was much higher than the DQI goal of 10% shown in Table A-3. The 2.16 ppm data may be off because the styrene concentration is very low and a small difference in the value as determined by the THC can result in a large percentage bias (a 5 ppm concentration of styrene in nitrogen was originally ordered). In retrospect, it would have been better to use a higher concentration, in the range of 15 ppm. The 170.8 ppm data are also low, by about the same percentage. However, in this case, line losses could be partly at fault because some condensation of styrene within a Teflon sample line had been observed in the past with this gas. In the air conditioned mobile lab, an unheated 2 m Teflon sample line was used.

For THC analyzer measurements in the sample van, bias was determined for each measurement of the 2.16 ppm span gases and is reported in Table A-5(b). At this concentration, average bias values for both analyzers were much greater than the target DQI of $\pm 5\%$. Partly, this is because a low value of styrene was sampled while the THC was calibrated with (what was thought to be) 52 ppm calibration gas. In retrospect, it would have been better to use a higher concentration, either lower than the calibration standard (in the range of 15 ppm) or higher than the calibration standard (in the range of 100 ppm). The single

sample of 170.8 ppm styrene calibration gas did show a much lower bias for both THC analyzers, below the expected DQI of 5%.

For THC analyzer measurements in the mobile lab, bias was determined for each measurement of the 850 ppm propane span gas and is reported in Table A-5(c). As with the values measured for precision, bias was very low, averaging less than 0.5% for both THC analyzers.

Completeness

For Method 18 samples, completeness was 100%. Some data were not usable because the molds that were sprayed during sampling runs when the video cameras malfunctioned could not be used to determine emissions per area of mold sprayed, but this was not related to the sampling effort.

For THC analyzer measurements made in the sampling van, completeness was 50% (for active spray booths). This is much lower than the DQI goal of 90%, but, data from these THC analyzers was only intended to back up data taken by the other set of THC analyzers in the mobile laboratory. For the THC analyzers in the mobile laboratory, a completeness of 91% was achieved (for active spray booths), essentially equal to the DQI goal of 90%. Together, both THC analyzers were able to obtain corroborative data for every Method 18 sample. With respect to THC samples taken to characterize styrene emissions not captured by active spray booths, 100% of the data needed to quantify non-spraying emissions was obtained by the THC analyzers in the mobile laboratory. It was not intended to utilize the THC analyzers in the sampling van as part of this effort although these instruments were able to contribute some of the emissions data measured during work day breaks at the active spray booths.

Representativeness

The physical layout of sampling locations at the Eljer facility dictated much of the sampling strategy and sampling methodology practiced during this evaluation to obtain representative samples. The use of heated sampling lines avoided condensation of styrene and the use of heated Tedlar bags also prevented condensation of styrene while the samples were being taken and subsequently analyzed. Location of the sampling line inlets near the center of exit vents assured that samples were representative. Following the

sample methodology recommended in EPA Method 18 also assured that representative samples were obtained.

Comparability

The sampling plan for this project made provision for simultaneous sampling using two measurement methods that should allow comparison of the results when suitably averaged over the same sampling period. In general, for THC analyzer-based measurements, styrene emissions from the lay-up booths and from the gel coat booths were much greater than those determined from Method 18 measurements. With the exception of the June 17 data, both methods measured essentially the same emissions from the single back-up booth. However, these differences do not suggest that the measurements are not comparable. Because standard deviations are relatively large for the lay-up and gel coat booths, the data do overlap.

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16. ABSTRACT The report gives results of emissions measurements, carried out at a representative facility (Eljer Plumbingware in Wilson, NC) that manufactures polyester-resin-reinforced shower stalls and bathtubs by spraying styrene-based resins onto molds in vented, open, spray booths. Styrene emissions were characterized for the three stages of manufacture by measuring styrene concentrations at the vents of spray booths used in each part of the process. In addition, styrene concentrations were measured at each ventilation fan exhaust. Emission levels were determined using EPA Method 18 to obtain integrated emissions samples and total hydrocarbon (THC) analyzers to measure continuous emissions levels during the EPA Method 18 sampling. Analysis of the EPA Reference Method data indicates that: (1) styrene monomer is the only volatile organic compound released in the process; (2) overall, approximately 4% of all material sprayed is lost to atmospheric emissions as styrene (approximately 19% of all styrene sprayed); and (3) emissions vary for each phase of manufacture, with post-spraying emissions of styrene (from curing molds) constituting a large part, approximately 29% of all emissions. (NOTE: Current EPA emission factors--AP-42--for styrene emissions from the production of polyester-resin-reinforced plastics represent a composite of spraying/post-spraying emissions.)		
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