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# EVALUATION OF A LIQUID CHEMICAL SCRUBBER SYSTEM FOR STYRENE REMOVAL



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EPA-600/R-94-211 December 1994

# EVALUATION OF A LIQUID CHEMICAL SCRUBBER SYSTEM FOR STYRENE REMOVAL

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### ABSTRACT

Manufacturing processes that involve the spraying of styrene-based resins have been identified as a possible significant source of volatile organic compound (VOC) emissions that may affect human health and contribute to the ozone non-attainment problem. Until recently, no known technology has been demonstrated to control such emissions of styrene. Now, several processes have been developed to control styrene emissions and a short-term field evaluation was planned to characterize the styrene removal efficiency of a pilot-scale version of a liquid chemical scrubbing process. This test was carried out at a facility (Eljer Plumbingware in Wilson, NC) that manufactures polyester bathtubs and shower stalls by spraying styrene-based resins onto molds in vented, open, spray booths. A side stream of air exhausted from one of the spray booths in the gel coating part of the process was used for this test.

In this study the styrene removal efficiency of a pilot-scale version of the QUAD Chemtact<sup>™</sup> scrubber was quantified by continuously measuring the total hydrocarbon (THC) content of spray booth exhaust air entering and exiting the device with THC analyzers and, for some tests, by collecting NIOSH EPA Method 18 samples (adsorption tube procedure) at the inlet and exit of the device. Twenty-five different combinations and strengths of scrubber chemicals (test conditions) were identified, and for each test condition, average styrene removal efficiency was determined. Average styrene removal efficiency approached but was never greater than 55% for any test condition.

This work was performed at the request of the Control Technology Center (CTC) steering committee to provide information to state and local agencies for use in responding to public concerns.

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# PREFACE

The Control Technology Center (CTC) was established by EPA's Office of Research and Development (ORD) and Office of Air Quality Planning and Standards (OAQPS) to provide technical assistance to state and local air pollution control agencies. Three levels of assistance can be accessed through the CTC. First, a CTC HOTLINE has been established to provide telephone assistance on matters relating to air pollution control technology. Second, more in-depth engineering assistance can be provided when appropriate. Third, the CTC can provide technical guidance through publication of technical guidance documents, development of personal computer software, and presentation of workshops on control technology matters.

The engineering assistance projects, such as this one, focus on topics of national or regional interest that are identified through contact with state or local agencies.

# Metric to Nonmetric Conversions

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

system.

Metric	Multiplier	Yields Nonmetric
kPa	1450.38	psig
kPa	4.0145	<b>in</b> . H <sub>2</sub> 0
°C	1.8T + 32	۰F
cm	0.3937	in.
m	3.2808	ft
m <sup>2</sup>	10.7639	ft <sup>2</sup>
m <sup>3</sup>	35.3134	tt <sup>3</sup>
mmHg	0.03937	in. Hg
kg	2.2026	łb
1000 kg	0.90802	ton
1	0.2643	gal.
m <sup>3</sup> /min	35.3134	ft <sup>3</sup> /min

## SECTION 1

## INTRODUCTION

The control of styrene is a major concern for many areas of the country. Up to the time of this evaluation, The Control Technology Center (CTC) had received over 30 calls on the topic. One area of styrene emissions is in the manufacture of shower stalls and bathtubs. There are approximately 200 of these plants operating in the U.S. emitting uncontrolled styrene to the atmosphere. Until recently, no known cost-effective technology had been demonstrated to control the emission of styrene.

After being contacted by one supplier of a styrene removal technology, the CTC attempted to find other vendors of control technology for styrene removal. One other vendor was found and the CTC contacted this vendor, QUAD Technologies Inc., of Chicago, IL, to propose the evaluation of their chemical scrubber process (the QUAD Chemtact<sup>™</sup> System) on a source of styrene emissions. This process utilizes liquid chemical scrubbing technology to remove styrene by spraying fine droplets (a mist) of a diluted chemical solution into a contaminated air stream as it is injected tangentially into the top of a hollow cylindrical reaction chamber. Styrene is apparently oxidized and absorbed into the mist of water and scrubber liquor which is continuously collected and exhausted through the chamber drain. The treated air is then exhausted tangentially through the bottom of the reaction chamber.

The CTC initiated a proposed project to evaluate processes for controlling styrene emissions at a representative fiberglass shower stall and bath tub manufacturing plant. Eljer Incorporated of Wilson, North Carolina was selected as a possible site and was visited by representatives of EPA in August of 1992 and later, in October, by representatives of EPA, SRI, and QUAD. A test was planned for November, 1992. However, due to scheduling constraints and equipment problems, this test was canceled. Later, in 1993, the test was rescheduled for June as part of a styrene emissions evaluation.

In May of 1993 a second site visit occurred and plans were finalized for the test in June. The week of June 21, 1993 was selected for the test.

This facility was selected because at this site Eljer manufactures both fiberglass shower stalls and bathtubs by spraying styrene-based resins onto various mold shapes in individual spray booths that are vented to the atmosphere. During the May visit, a tentative agreement was reached to test the Chemtact process on a representative source of styrene emissions from the shower stall/bathtub construction process.

Vent air from the spray booths used for mold-coating that is exhausted to the atmosphere is the major point source of emissions from the manufacture of fiberglass shower stalls and bathtubs. Thus, the number of manufacturing steps that involve the spraying of styrene-based resins and the number of individual spray booths in operation at a particular facility determine the level of styrene emitted to the atmosphere.

Any fiberglass product that during its manufacture requires the spraying of styrene is a source of organic vapors that could affect human health both directly and indirectly. The results of this evaluation will provide information to state and local agencies for use in responding to public concerns.

### SECTION 2

## **PROJECT DESCRIPTION**

#### 2.1 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 is mixed with polyester resin and a pigment to create a "gel coat" that is sprayed onto a previously prepared mold. Molds are typically 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 coated mold is set aside while the resin is allowed to cure. Because curing is an exothermic process, the next manufacturing step is usually not carried out until the coated mold has cooled. Fiberglass provides structural support for the finished article, styrene and polyester resin act as a glue to hold the matrix together, and the inert fillers provide additional structural support and can also serve as a fire retardant. The final step of manufacture is to separate the finished fiberglass product from the mold and prepare the product for shipment.

The purpose of this project was to evaluate the performance of a pilot-scale liquid chemical scrubber designed to control styrene emissions. During this evaluation, the pilot-scale control device was configured to treat a portion of the air exhaust from a gelcoat booth at a fiberglass shower stall and bath tub manufacturing plant operated by Eljer Plumbingware located in Wilson, North Carolina.

To measure the styrene removal efficiency of the pilot-scale liquid chemical scrubber, total hydrocarbon (THC) analyzers equipped with flame ionization detectors (FID) were used to determine total hydrocarbon levels at the inlet and outlet of the device on a continuous basis while charcoal-filled sampling tubes were used to collect samples of volatile organic compounds (VOC's) at the inlet and outlet of the device over time periods of approximately one-half hour. Styrene levels in the inlet and outlet gas streams were quantified by subsequent chromatographic analysis (with FID detection) of the VOC's retained in the charcoal-filled sampling tubes.

### 2.2 ELJER PLUMBINGWARE FACILITY

The Eljer Plumbingware facility, diagrammatically shown in Figure 1, is located in Wilson, North Carolina. In this figure the location of the pilot-scale scrubber is shown along with the location of the van used for sampling. During this evaluation, the workday started at 0700. Breaks in production occurred at 1000 hours (15 minute morning break) and 1200 hours (30 minute lunch break). The workday ended at 1400.

Each stage of manufacture except for mold separation or "pulling" begins in a spray booth. At the Eljer facility the spray booths were not constructed in place but are prefabricated units manufactured by Binks, Inc. Each spray booth is approximately 3.05 m (10 ft) high, 4.11 m (13.5) ft wide, and approximately 3.66 m (12 ft) deep. 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.

Each spray booth is continuously vented with air from the interior of the plant that is pulled into the booth entrance, through the air conditioning filter mat, and a five-blade fan unit mounted approximately 2m below the roof of the building. Air pulled into the fan exits through ductwork that reenters the side of the building and exhausts 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 m<sup>3</sup>/min (14,500 acfm).

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 gelcoat spray booths located in 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 (32.2% styrene by analysis) and is purchased as a prepared mix in 55 gallon drums and, during this test, contained no



Figure 1. Layout of Eljer Plumbingware Facility

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 m<sup>2</sup>) with gel coat and five minutes are required to coat a large shower stall mold (7-8 m<sup>2</sup>) with gelcoat. When spraying is complete, the mold is oriented upright and the pedestal is lowered until the wheeled cart mounted to the mold contacts the floor. The mold and 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 (21.4% styrene by analysis). 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 in this stage and during spraying, 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 an 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 or "roll" 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). 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 (20.9% styrene by analysis). 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.

This back-up mixture is also sprayed with chopped fiberglass fibers and forms the final two layers of the mold. 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.

The final stage 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.

## 2.3 THE LIQUID CHEMICAL SCRUBBING PROCESS

The liquid chemical scrubbing process that was the subject of this evaluation was originally developed for odor control.<sup>1</sup> Subsequent to this development, it was determined by the manufacturer that a system of this type could be used to control VOC emissions. The following description of the liquid chemical scrubbing process is taken from general information supplied by the manufacturer on the operation of the liquid chemical scrubbing process. No specific information was provided that described how a full-scale version of this system operates or how a full-scale system differs from the pilot-scale

This technology takes advantage of a patented absorption technique based on the mass transfer equation that provides enhanced chemical reactivity with an atomized mist. The manufacturer asserts that mist provides a large surface area where gas-liquid phase reactions take place that result in the elimination of gaseous contaminants.

Figure 2 shows a schematic diagram of a vertically-configured liquid chemical scrubbing device that incorporates all of the equipment necessary to operate as a stand-alone unit. Because of design considerations, the components of a full-scale unit would probably be arranged in a horizontal configuration. The major components of such a system are an air compressor, a continuous monitor for pH control of the scrubber liquor, a water softening unit, scrubber chemicals with chemical metering pumps, the scrubber reaction chamber with its associated spray nozzle, the exhaust fan, and the outlet stack. This is a once-through process. Thus, spent scrubber liquids are disposed of and are not regenerated. Literature supplied by the manufacturer does not indicate if the liquid effluents generated by this process require special handling for their disposal.

Styrene is removed by spraying fine droplets of a diluted chemical solution into a contaminated air stream as it passes through a hollow, cylindrical reaction chamber. Spray nozzles are situated within the chamber so that a fog of chemical-containing droplets mixes with the incoming contaminated air and flows in the same direction toward the outlet. The mixing process in the chamber is enhanced by the tangential inlet that forces a swirling motion within the chamber. As the mixture travels through the reaction chamber, the chemical-containing droplets solubilize or absorb and react with VOC's in the contaminated air stream. Treated air is exhausted tangentially from the bottom of the chamber. It then proceeds to another chamber (not shown in Figure 2) or to the exhaust stack. After solubilization or reaction has taken place, unevaporated droplets that are large enough to be captured on the sides of the reaction chamber collect at the drain opening in the floor of the chamber and are discharged. A pH sensor located in the drain piping is used as a control input to maintain the pH of the liquid effluent's at a preset value. In a large unit suction pressure is usually maintained at 0.25 kPa (1 in. H<sub>2</sub>O). These units are constructed from PVC or fiberglass.



Figure 2. Diagrammatic representation of the liquid chemical scrubbing process.

## 2.3.1 Pilot-Scale Liquid Chemical Scrubbing Device

A diagram of the pilot unit is shown in Figure 3. In this figure, styrene-laden air enters at the top right, and successively passes through each of the three reaction chambers. The chambers and all interconnecting tubing are constructed of PVC plastic. The reaction chambers are nominally 1.07 m (3.5 ft) in diameter and 1.83 m (6 ft) high. Interconnecting PVC piping has a nominal inside diameter of 8.9 cm (3.5 in.). In each reaction chamber, contaminated air enters tangentially at the top of the chamber and mixes with a mist of the scrubbing liquor that is sprayed from three titanium spray nozzles within the chamber. The tangential inlet forces air and mist to swirl together while it transits the chamber. The air and mist exit through a similar tangential outlet at the bottom of the chamber and flow through two 90° bends before entering at the top of the next reaction chamber. Each reaction chamber has a bottom drain that, for this test, was exhausted into a plastic bucket. At the exit of the last reaction chamber the mist and air stream pass through a 90° bend upward to an exhaust fan that is vented to the atmosphere.

The atomizing nozzles are designed to operate at choked flow (sonic velocity) when supplied with compressed air at a pressure of 413.7 kPa (60 psig). As Figure 3 shows, the pilot unit was equipped with three identical reaction chambers (in series) that have tangential top inlets and tangential outlets at three vertical elevations. Only the bottom outlets were used during this test. Also shown in Figure 3 are the locations used to obtain inlet and outlet gas samples as well as the location of the pressure taps used to measure system pressure drop.

Each reaction chamber was fed by a separate chemical metering pump so that a contaminated air stream could be treated with up to three different chemical solutions as it passed through the device. Separate five gallon plastic buckets were used to mix and hold the chemical solutions that were supplied to each metering pump.

The manufacturer states that most of the fine droplets collect at the drain opening cast into the floor of each reaction chamber where the collected liquid is exhausted. Thus, there should be little liquid carryover. This was observed to be the case during testing.



Figure 3. Diagram of the pilot-scale liquid chemical scrubber tested at Eljer Plumbingware.

# 2.3.2 Specific Test Conditions

Throughout this evaluation the pilot unit was operated at a slight negative pressure, from 0.8 to 0.9 kPa (3.2 to 3.6 in. H<sub>2</sub>O) at a nominal flow rate of 2.0 m<sup>3</sup>/min (70 acfm). Laundry bleach (NaClO), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), and ethylene glycol (antifreeze) along with a variety of surfactants were evaluated for styrene removal.

Table 1 presents the overall conditions encountered for the three days of testing. Tables 2 through 4 delineate the specific test conditions, scrubber additives, and flows used in each reaction chamber of the liquid chemical scrubber for each day of testing, June 22 through June 24, 1993. Entries in Tables 2 though 4 are listed in chronological order, starting with the first mold that was sprayed while the liquid chemical scrubber was operational through to the end of the day of testing. As can be seen from an inspection of these tables, a number of test conditions were tried. This was because styrene removal efficiency across the liquid chemical scrubber was never very great, which led to the trial of a variety of scrubber additives, and because it was easy to change from one scrubber additive to another for a particular reaction chamber.

It is difficult to comment on the choice of scrubber additives and surfactants used by the scrubber manufacturer, particularly because the manufacturer has not provided any information as to why the additives and surfactants that were used were chosen for testing. Given the relatively poor performance that was observed, the matter was not pursued.

Table 1.	Daily Test Conditions	

Date	Time	Inlet Air Temp.	Rel. Humidity	Bar. Pressure	System ∆P	Air Flow Rate
	ł		(%)	(KPa)	(KPa)	<u>(m²/min)</u>
June 22	0810	26.7	82	101.1	0.80	2.01
June 23	0734	21.1	72	101.4	0.80	1.86
	1345	37.8	42	102.2	0.80	1.88
June 24	0719	22.2	80	102.2	0.87	1.97
	1217	37.8	40	102.9	0.90	1.64

<u> </u>				Scrubber	Additio	n Rate	Scrubber	Additio	n Rate	Scrubber	Additio	n Rate
Test	Mold	Start	End	Reaction	Additive	Water	Reaction	Additive	Water	Reaction	Additive	Water
Cond.	#	Time	Time	Chamber #1	(lph)	(lph)	Chamber #2	(lph)_	(lph)	Chamber #3	(lph)	(lph)
				_								
1	1	0834	0839	H <sub>2</sub> O	0.96	11.36	No Spraying	0.00	0.00	No Spraying	0.00	0.00
	2	0844	0850	H <sub>2</sub> O	0.96	11.36	No Spraying	0.00	0.00	No Spraying	0.00	0.00
	3	0853	0859	H <sub>2</sub> O	0.96	11.36	No Spraying	0.00	0.00	No Spraying	0.00	0.00
	4	0903	0907	H <sub>2</sub> O	0.96	11.36	No Spraying	0.00	0.00	No Spraying	0.00	0.00
2	5	0908	0916	Antifreeze	0.96	11.36	No Spraying	0.00	0.00	No Spraying	0.00	0.00
1	6	0920	0925	Antifreeze	0.96	11.36	No Spraying	0.00	0.00	No Spraying	0.00	0.00
3	7	0931	0942	Antifreeze	0.96	11.36	NaCIO (5.25%)	2.56	11.36	No Spraying	0.00	0.00
1	8	0947	0956	Antifreeze	0.96	11.36	NaCIO (5.25%)	2.56	11.36	No Spraying	0.00	0.00
	9	0957	1002	Antifreeze	0.96	11.36	NaCIO (5.25%)	2.56	11.36	No Spraying	0.00	0.00
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	11	1043	1047	Off Line	-	-	Off Line	-	-	Off Line	-	-
	12	1051	1100	Off Line	-	-	Off Line	- 1	- 1	Off Line	-	-
	13	1101	1108	Off Line	-	-	Off Line	- 1	-	Off Line	-	-
5	14	1117	1124	Antifreeze	0.96	37.85	NaCIO (5.25%)	2.56	37.85	H <sub>2</sub> O Only	0.00	37.85
	15	1130	1135	Antifreeze	0.96	37.85	NaCIO (5.25%)	2.56	37.85	H <sub>2</sub> O Only	0.00	37.85
	16	1138	1146	Antifreeze	0.96	37.85	NaCIO (5.25%)	2.56	37.85	H <sub>2</sub> O Only	0.00	37.85
	17	1147	1155	Antifreeze	0.96	37.85	NaCIO (5.25%)	2.56	37.85	H <sub>2</sub> O Onty	0.00	37.85
6	18	1239	1243	NaCIO (5.25%)	1.50	34.07	NaCIO (5.25%)	2.56	34.07	H <sub>2</sub> O Only	0.00	34.07
7	19	1259	1305	NaClO (5.25%),	1.50	34.07	NaCIO (5.25%)	2.56	34.07	H <sub>2</sub> O Only	0.00	34.07
1				NaOH (2.4%)			_	1				
	20	1308	1312	NaCIO (5.25%),	1.50	34.07	NaCIO (5.25%)	2.56	34.07	H <sub>2</sub> O Only	0.00	34.07
	24	1212	1210	NaOH (2.4%)	1.50	34.07	NaCIO (5.25%)	2.56	34 07	H <sub>e</sub> O Only	0.00	34.07
l °	21	1313	1310	NaOH (2.4%)	1.50	34.07		1	54.07	1120 01119	0.00	04.01
				Surfactant "E"								
[	22	1322	1328	NaCIO (5.25%),	1.50	34.07	NaCIO (5.25%)	2.56	34.07	H <sub>2</sub> O Only	0.00	34.07
				NaOH (2.4%),								
	~	(220		Surfactant "E"	1.50	24.07		255	24.07	H-O Only	000	34.07
А	23	1338	1342	NaCIU (3.23%), Surfactant "F"	1.50	34.07	Surfactant "F"	2.50	34.07	120 Uliy	0.00	J=4.07
	24	1351	1356	NaCIO (5,25%).	1.50	34.07	NaCIO (5,25%).	2.56	34.07	H <sub>2</sub> O Only	0.00	34.07
				Surfactant "E"			Surfactant "E"			• • • •		

Table 2. Summary of Test Conditions for June 22, 1993

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H2SO4 (2%)         H2SO4 (2%)           12         0939         0945         Nacio (5 25%) + 0 90         34.07         Nacio (5 25%) + 1.70         34.07         H2O Only         0.00           12         0939         0945         Nacio (5 25%) + 0 90         34.07         Nacio (5 25%) + 1.70         34.07         H2O Only         0.00           12         0939         0945         Nacio (5 25%) + 0 90         34.07         Nacio (5 25%) + 1.70         34.07         H2O Only         0.00           10         Reach pH = 7         to Reach pH = 7         to Reach pH = 7         10	34.07
12         0939         0946         Nacio (5 25%) + H <sub>2</sub> SO <sub>4</sub> (2%)         0 90         34.07         Nacio (5 25%) + H <sub>2</sub> SO <sub>4</sub> (2%)         1.70         34.07         H <sub>2</sub> O Only         0.00	
12         0939         0945         Surfactant "B"         Surfactant "B"         1.70         34.07         H <sub>2</sub> O Only         0.00           12         0939         0945         NaCiO (5 25%) +         0.90         34.07         NaCiO (5 25%) +         1.70         34.07         H <sub>2</sub> O Only         0.00           12         0939         0945         NaCiO (5 25%) +         0.90         34.07         NaCiO (5 25%) +         1.70         34.07         H <sub>2</sub> O Only         0.00           12         0939         0945         NaCiO (5 25%) +         0.90         34.07         H <sub>2</sub> O Only         0.00           12         0939         0945         NaCiO (5 25%) +         0.90         H <sub>2</sub> SO <sub>4</sub> (2%)         1.70         34.07         H <sub>2</sub> O Only         0.00	
12 0939 0946 NaCiO (5 25%) + 0 90 34.07 NaCiO (5 25%) + 1.70 34.07 H <sub>2</sub> O Only 0.00 H <sub>2</sub> SO <sub>4</sub> (2%) H <sub>2</sub> SO <sub>4</sub> (2%) H <sub>2</sub> SO <sub>4</sub> (2%) 0.00 to Reach pH =7 to Reach pH =7.	
H <sub>2</sub> SO <sub>4</sub> (2%) H <sub>2</sub> SO <sub>4</sub> (2%) to Reach pH =7 to Reach pH =7.	34.07
I I I I I I I I I I I I I I I I I I I	
Surfactant "B" Surfactant "B"	
6 13 0948 0955 H <sub>2</sub> SO <sub>4</sub> (2%), 0.90 34.07 H <sub>2</sub> SO <sub>4</sub> (2%), 1.70 34.07 H <sub>2</sub> O Only 0.00	34.07
Surfactant "A" Surfactant "A"	0.07
7 14 1031 1036 $H_2SO_4$ (2%), 0.90 34.07 $H_2SO_4$ (2%), 1.70 34.07 $H_2OONY$ 1.85	34.07
Surfactant "E" Surfactant "E"	24.07
8 15 1039 1048 H2SO4 (2%), 0.90 34.07 H2SO4 (2%), 1.70 34.07 Surractant P 1.86	34.07
Surfactant "E" Surfactant "E" A 70 0407 Surfactant TE" 1 90	24.07
$16 1049 1057 H_2SO_4 (2%), 0.90 34.07 H_2SO_4 (2%), 1.70 34.07 Surractant F 1.85$	34.07
Surfactant "E" Surfactant "E" 4.70 04.07 Outpatient "D" 4.80	24.07
9 17 1101 1105 $H_2SO_4(2.6)$ , 0.90 34.07 $H_2SO_4(2.6)$ , 1.70 34.07 Surractant D 1.65	34.07
A THE THE SUMECIANT E SUMECIANT E	34.07
18 1112 1120 H2SU4 (2%), 0.90 34.07 H2SU4 (2%), 1.70 34.07 Surractant 0 1.88	34.07
	34.07
	34.07
	34.07
21 115/ 12:03 H2:04 (276) 0.50 34.07 H2:04 (276) 1.70 34.07 H2:04 (276) 1.85	34.07
11 22 1242 1254 NaCIO (5,25%), 0.90 34.07 NaCIO (5,25%), 1.70 34.07 H <sub>2</sub> O Only 0.00	34.07
to an international surface and a surface and the surface and	34.07
12 23 1259 1306 NaClO (5.25%), 0.90 34.07 NaClO (5.25%), 1.70 34.07 H <sub>2</sub> O Only 0.00	34.07
Cold Dil, Water Cold Dil, Water	24.07
24 1308 1313 NaCIO (5.25%), 0.90 34.07 NaCIO (5.25%), 1.70 34.07 H <sub>2</sub> O Only 0.00	34.07
	24.07
25 1317 1322 NaCIO (5.25%), 0.90 34.07 NaCIO (5.25%), 1.70 34.07 H2O OTTY 0.00	34.07
	24.07
13 26 1324 1327 H2SU4 (2%), 0.00 34.07 Hacilo (5.25%) 2.56 34.07 H2C Only 0.00	54.07
77 1000 1007 H SO (28) 0 SO 34 07 Nocio (5 258) 2 SS 34 07 H O Only 0 D	34.07
2/ 1332 1337 m2504 (27), U.OU 34.07 matrix (5.25%) 2.50 34.07 m20 0mg U.OU	0.07
	34.07
20 1340 1344 H2504 (27), 0.00 34.07 NaCIO (3.23%) 2.30 34.07 H20 Only 0.00	J
	1. 1
	1 34 07
20 1077 1000 H SO (28) 0.60 24.07 NoClo (5.25%) 2.66 34.07 H-0.05% 0.00	34.07
JU 130/ 1403 [12004 (270), U.OU [34.07] (14010 (0.2376) 2.30 [34.07] (120 Offly 0.00	34.07 34.07

Table 3. Summary of Test Conditions for June 23, 1993

				Scrubber	Additio	n Rate	Scrubber	Additio	n Rate	Scrubber	Additio	n Rate
Test	Mold	Start	End	Reaction	Additive	Water	Reaction	Additive	Water	Reaction	Additive	Water
Cond.	#	Time	Time	Chamber #1	(liph)	(lph)	Chamber #2	(lph)	(lph)	Chamber #3	(lph)	(iph)
								1				-
1	1	0742	0748	$H_2O_2$ (3%)	1.06	34.07	$H_2O_2(3\%)$	1.25	34.07	$H_2O_2(3\%)$	1.14	34.07
,	4	0805	0800	$\Pi_2 U_2 (376)$	1.00	34.07	Mater	0.00	34.07	Water	0.00	34.07
1	4	0813	08108		1.06	34.07	Water	0.00	34.07	Water	0.00	34.07
	5	0822	08208	Dilute MEKP	1.06	34.07	Water	0.00	34.07	Water	0.00	34.07
3	6	0837	0842	H2SO4 (2%),	1.05	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07
	7	0847	0853	H <sub>2</sub> SO <sub>4</sub> (2%), Surfactant "E"	1.05	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07
	8	0857	0903	H <sub>2</sub> SO <sub>4</sub> (2%),	1.05	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07
	9	0905	0911	H <sub>2</sub> SO <sub>4</sub> (2%), Surfactant "E"	1.05	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07
	10	0912	0920	H <sub>2</sub> SO <sub>4</sub> (2%), Surfactant "F"	1.05	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07
	11	0932	0937	H <sub>2</sub> SO <sub>4</sub> (2%), Surfactant "E"	1.05	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07
	12	0 <b>9</b> 40	0948	H <sub>2</sub> SO <sub>4</sub> (2%), Surfactant "E"	1.05	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07
	13	0953	1000	H <sub>2</sub> SO <sub>4</sub> (2%), Surfactant "E"	1.05	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07
	14	1034	1039	H <sub>2</sub> SO <sub>4</sub> (2%), Surfactant "E"	1.05	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07
	15	1044	1053	H <sub>2</sub> SO <sub>4</sub> (2%), Surfactant "E"	1.05	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07
	16	1054	1101	H <sub>2</sub> SO₄ (2%), Surfactant "E"	1.05	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07
	17	11 <b>0</b> 6	1112	H <sub>2</sub> SO <sub>4</sub> (2%), Surfactant "E"	1.05	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07
	18	1118	1124	H <sub>2</sub> SO <sub>4</sub> (2%), Surfactant "E"	1.05	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07
	19	1128	1134	H <sub>2</sub> SO <sub>4</sub> (2%), Surfactant "E"	1.05	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07
	20	1138	1141	H <sub>2</sub> SO <sub>4</sub> (2%), Surfactant "E"	1.05	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07
	21.	1146	1153	H <sub>2</sub> SO <sub>4</sub> (2%), Surfactant "E"	1.05	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07
	22	1156	1206	H <sub>2</sub> SO <sub>4</sub> (2%), Surfactant "E"	1.05	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07
	23	1244	1247	H <sub>2</sub> SO <sub>4</sub> (2%), Surfactant "E"	1.05	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07
	24	1252	1257	H <sub>2</sub> SO <sub>4</sub> (2%), Surfactant "E"	1.05	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07
	25	1333	1338	H <sub>2</sub> SO <sub>4</sub> (2%), Surfactant "E"	1.05	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07
	26	1339	1344	H <sub>2</sub> SO <sub>4</sub> (2%), Surfactant "E"	1.05	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07
	27	1346	1350	H <sub>2</sub> SO <sub>4</sub> (2%), Surfactant "E"	1.05	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07
	28	1352	1353	H <sub>2</sub> SO <sub>4</sub> (2%), Surfactant "E"	1.05	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07
					1		L	1	1			L

Table 4. Summary of Test Conditions for June 24, 1993

# 2.4 EXPERIMENTAL APPARATUS

## 2.4.1 Connection to the Pilot-Scale Liquid Chemical Scrubber

The pilot-scale device was situated as close as possible to the outlet of Gel Coat booth #2 located on the roof of the facility. A 15.24 cm (6 in.) diameter flexible aluminum sampling line was used to convey a sample of air exiting the spray booth. This line was approximately 17.1 m (56 ft) long. This sampling line was not heat-traced because local ambient temperatures averaged near 38°C (100°F) during most of the testing. At the exit of the last reaction chamber but before the exhaust fan a tee was connected to the nominal 10.2 cm (4 in.) diameter PVC exhaust line to obtain outlet air samples. Because saturated air and some mist exited the last reaction chamber, the outlet sample line contained a liquid drop out section that was drained as needed. Figure 4 shows how the pilot unit and the van containing the sampling equipment were situated.

At the pilot unit inlet and outlet single 9.53mm (0.375 in.) diameter heated Teflon® sample lines were used to carry gas samples to the sample van for analysis. The inlet sample line was about 2.13 m (7 ft) long. The outlet sample line was approximately 3.66 m (12 ft) long with the condensate trap placed midway in the line at its lowest point.

The EPA Quality Assurance Handbook applicable to Method 18 sampling indicates that it is proper to maintain sampling lines above the local ambient temperature if the compound being sampled could condense within the sample lines.<sup>2</sup> Thus, to avoid the possibility of styrene loss and to minimize condensation of water from the saturated air in the outlet sampling line, the sample lines were heated to at least 11°C (20°F) above the local ambient temperature. Because the local afternoon temperature averaged near 38°C (100°F) during the test, all sample lines were kept at 49°C (120°F).

## 2.4.2 Sampling Van

Figures 5 and 6 show how the gas sampling equipment was connected within the van used to house the sampling equipment. Two equivalent systems were constructed so that concurrent samples could be obtained at the inlet and the outlet of the liquid chemical scrubber. Thus, the description that follows applies to either system.



Figure 4. Overall arrangement for sampling at the Eljer Plumbingware Facility



Figure 5. Equipment Arrangement Used for Sampling with THC Analyzers



Figure 6. Equipment arrangement used for EPA Method 18 sampling.

Shortly after each 9.53mm diameter sample line entered the sampling van it was divided into two 6.35 mm (0.25 in.) diameter sample lines less than 10 cm in length. The smaller sampling lines were not heat traced. One line was connected to a J.U.M. Instruments VE-7 THC analyzer and the other line was connected to a Swagelock<sup>™</sup> "Tee" connector with a shut off-valve from which samples of gas could be withdrawn into charcoal-filled adsorption tubes (EPA Method 18, Section 7.4 or NIOSH Method 1501). Outlet charcoal tube samples were preceded by an anhydrous sodium sulfate-filled drying tube to remove water vapor. Sample flow was maintained at 3 1/m by the THC analyzer. When EPA Method 18 samples were taken this flow was increased by 0.2 1/m at the inlet and 0.5 1/m at the outlet. With the short sample lines this flow rate was more than sufficient to assure that residence times in the sample lines were low (between 2 and 3 seconds for the longest sample line).

Figure 5 shows the calibration gas system used for the THC analyzers. Three mixtures of styrene in nitrogen were used for calibration (171 ppm, 39 ppm, and 2.2 ppm), in addition to zero air (less than 0.1 ppm THC). The bottles of calibration gas were interconnected with positive shut-off valves to a common manifold that was itself connected to the span gas port on both THC analyzers. This system allowed both THC analyzers to be calibrated from the same calibration gases.

It should be noted that after all testing had been completed, concentrations of the styrene gases used for calibration standards during testing (from the vendor that supplied the gases, Matheson Gas Products, Inc.) were found to be in substantial error. The values quoted above were determined separately as part of a process that established that the vendor-supplied calibrations were in error. Appendix B, the Quality Control Evaluation Report for this work, details this process and the method used to correct the field THC data.

The 0 - 10 V output signal from each THC analyzer was fed to one channel of a two-channel chart recorder. The output signal from each THC analyzer was also recorded on 1.44 Mb floppy disks with a dedicated PC-based datalogger. Output from each THC analyzer was logged once every second. The software used to log the data (Quicklog PC<sup>™</sup>) was configured to display the last 50 minutes of data

(last 3000 data values) from both channels on the PC monitor. Output from the inlet THC analyzer was displayed on a 0 to 1000 ppm scale and output from the outlet THC analyzer was displayed on a 0 to 100 ppm scale.

Previously it had been determined that virtually all (99%) of the organic material exhausted from the gelcoat spray booths was styrene monomer.<sup>3</sup> In this case, as for previous testing at this facility, the primary intent of these measurements was to establish time-averaged levels of styrene at the inlet and outlet of the pilot-scale styrene control device to determine the styrene removal efficiency. As with previous measurements, EPA Method 18 (adsorption tube procedure, equivalent to NIOSH Method 1501) was followed in obtaining these samples (see Appendix A).<sup>3</sup>

Figure 6 shows the equipment arrangement used for the EPA Method 18 sampling. The same basic arrangement was used to obtain inlet and outlet samples except that at the outlet each adsorption tube was preceded by a drying tube that contained anhydrous sodium sulfate. It was necessary to provide dry, or relatively dry, air to the charcoal adsorption tubes used in this test because the adsorption efficiency of styrene (on charcoal) drops off sharply as absolute humidity increases (see Appendix A). Anhydrous sodium sulfate is widely used for this type of sampling and does not collect styrene. The samples were obtained with a single volatile organic sampling train (VOST) sampling pump connected to a manifold that, in turn, was connected to a standard small charcoal-filled tube. Flow was set before each measurement to approximately 0.2 1/m for inlet samples and 0.5 1/m for outlet samples.

#### 2.5 EXPERIMENTAL METHODS AND PROCEDURES

#### 2.5.1 Total Hydrocarbon Analyzers

J.U.M. Instruments Model VE-7 total hydrocarbon (THC) analyzers equipped with flame ionization detectors (FID) were used to obtain a continuous measurement of the total hydrocarbon content in air that entered (air exhaust from gelcoat booth #2) and exited the pilot-scale liquid chemical scrubber. This analyzer extracts approximately 31/m of sample with an internal sample pump

and sends from 17 to 20 cm<sup>3</sup>/m of that sample to an onboard FID. The FID's in these instruments were set up to use a 60% helium- 40% hydrogen (helifuel) mixture as a tuel. Two of these THC analyzers were used for the duration of testing. These instruments were inspected and were zeroed and calibrated with THC-free air and the styrene span gases respectively before testing.

The JUM VE-7 provides five decade output ranges that can be manually selected from 0-10 ppm to 0-100,000 ppm. A 0-10V signal is output at the rear of the instrument that corresponds to the decade range selected. The instrument used to sample air from the inlet of the liquid chemical scrubber was set to measure in the 0-1000 ppm range and the instrument used to monitor air exhausted from the device was set to measure in the 0-100 ppm range. As indicated above, the output from each of these instruments was recorded on a two-channel chart recorder and also logged on a dedicated PC-based data acquisition system.

These instruments are normally calibrated with propane. However, for this test they were calibrated with three mixtures of styrene in nitrogen (171 ppm, 39 ppm, and 2.2 ppm) in addition to zero air (less than 0.1 ppm hydrocarbons). When the instruments were zeroed on zero air, Instrument response was linear with the three calibration gases.

The instruments were calibrated and operated according to the manufacturer's instruction manual. Calibration and zero gas connections on the back panel of the instrument were not used, rather calibration and zero gas were routed to the sample gas input (common field practice), and calibration and zero gas pressures were maintained at sample gas input pressure levels. Fuel gas (helifuel) pressure was maintained at 1.5 bar (21 psig). Internal instrument sample pressure was maintained at 200 mbar (3 psig). Full calibrations (all span gases, zero gas) were performed on both THC analyzers at the beginning and middle of each day and instrument calibration was checked at the end of each day of testing.

### 2.5.2 Collection of EPA Method 18 Samples

The Adsorption Tube Procedure defined in Section 7.4 of EPA Method 18 (equivalent to NIOSH Method 1501) was followed to obtain samples of VOCs from air that entered the liquid chemical scrubber (air exhaust from gelcoat booth #2), air that exited the device, and from the low and midrange

styrene calibration standards. EPA Method 18 (Adsorption Tube Procedure) specifies that an applicable NIOSH Method be followed for the analysis of such samples. A copy of the proper NIOSH procedure (NIOSH Method 1501) is included in Appendix A.

As shown in Figure 6, the heated inlet and outlet sampling lines were divided after reaching the van housing the sampling equipment. One side was directed to a THC analyzer and the other side to a VOST sample pump through a stainless steel fitting where VOC samples were taken. Flow through the VOST pump was set at 0.2 I/m for inlet samples and at 0.5 I/m for outlet samples. Thus, total sample flow was 3.2 I/m at the inlet and 3.5 I/m at the outlet. A higher sample flow was used at the outlet to be sure that sufficient styrene would be captured in the adsorption tube for proper analysis. Sample times ranged from 19 to 32 minutes and were governed by process stability. Originally it was planned to take many more samples than were obtained. However, this was prevented due to difficulties encountered in the operation of the pilot-scale liquid chemical scrubber and the large number of short-duration test conditions.

Because air at the outlet of the pilot-scale device was saturated with water, provision had to be made to remove water from air samples before the air reached the charcoal-filled adsorption tubes (SKC Model 226-01 coconut charcoal-filled tube, NIOSH approved, Lot 120). This is because the styrene collection efficiency of the coconut charcoal in the adsorption tubes is severely degraded by the presence of water vapor under conditions of high humidity (see Appendix A). Therefore, the charcoal-filled adsorption tubes were preceded by standard drying tubes filled with 9 grams of anhydrous sodium sulfate (SKC Catalog No. 226-44-02). Anhydrous sodium sulfate does not adsorb or react with styrene vapor. Large-capacity tubes were used to insure that all of the water in the incoming air stream would be removed and because the other size available (250 mg) did not provide a sufficient margin of safety for water vapor removal. One of the large-capacity tubes can remove all of the water from approximately 200 I of 35°C (95°F) saturated air. In this sampling effort these drying tubes were used once and then discarded. Sample volume never exceeded 16 I.

Samples of the styrene calibration gases were taken directly from the gas cylinders. For these samples, flow was measured with a Buck Model M-5 primary gas flow standard bubble flow meter.

Sample volumes and total styrene loadings were kept within the ranges established by EPA Method 18 and NIOSH Method 1501 (see Appendix A).

To prevent contamination, all sample tubes are made of glass and are designed so that a small glass seal on either end of the tube must be broken off before a gas sample can be pulled through the tube. Samples were taken over time periods ranging from 19 to 32 minutes. When sampling ended each tube was sealed with a plastic cap provided by the manufacturer. Previous experience at SRI has shown that when styrene is sampled, these tubes do not require refrigeration to preserve the sample prior to analysis. Thus, the tubes were kept at room temperature until their contents were extracted for analysis. Previous experience at SRI has also shown that these tubes can await extraction for up to three weeks with no noticeable degradation in sample recovery and that such samples do not require refrigeration while analysis is pending. However, all of the charcoal sample tubes taken for this study were analyzed well within three weeks after they were obtained.

The charcoal-filled sample tubes from this evaluation were returned to SRI's laboratories in Birmingham, Alabama for analysis. Analysis consisted of desorption of VOC's adsorbed on the charcoal with carbon disulfide (according to the EPA Method 18 mandated NIOSH procedure that is proper for styrene detection, NIOSH Method 1501, reproduced in Appendix A) followed by injection into a gas chromatograph (GC) coupled to an FID. In addition, styrene standards were used to spike randomly selected charcoal-filled tubes and these samples were analyzed to determine a desorption efficiency specific to this lot of charcoal-filled tubes (in this case, 90.25%). From this analysis, styrene present in the samples was quantified. Knowledge of the amount of styrene present, the sample time, and the sample gas flow rate allowed the determination of a time averaged value for the styrene present at the inlet and outlet of the control device that could be compared with data from the THC analyzers.

### 2.5.3 Collection of Scrubber Liquid Samples

Samples of spent scrubber liquid were obtained from the first two reaction chambers on June 23 (at 1340) and from all three reaction chambers on June 24 (at 1040). On June 23, only water was injected in the third reaction chamber so no liquid sample was taken. In addition, a sample of the tap (process) water used to dilute the chemicals used for scrubbing was obtained on June 24 (at 1015). All

liquid samples were preserved in 250 ml glass sample bottles with Teflon-sealed caps. The samples were kept at room temperature, away from light.

The liquid samples were brought back to SRI's Birmingham, Alabama laboratories where, according to the standard operating procedure for water samples, they were refrigerated until they could be analyzed (refrigeration was not required in the field). Each liquid sample was diluted and subjected to chromatographic analysis for the presence of volatile and semivolatile organic compounds. The results of these analyses are shown in Appendix D. Some of these analyses were complicated by surfactants (intended to improve droplet dispersion) that were present in the scrubber liquid samples. During analysis these surfactants tended to produce copious amounts of foam.

### 2.5.4 Total Flow Rate Measurements

It was planned to make daily measurements of the total flow rate into the pilot-scale liquid chemical scrubber with a standard pitot tube according to EPA Method 1A. However, the flow rate into this device was determined to be much lower than was expected, too low to measure accurately with a standard pitot. Thus, on June 22, after it was determined that the standard pitot would not be useable, arrangements were made to obtain a thermal anemometer that had been calibrated in a wind tunnel at SRI's laboratories in Birmingham, Alabama. On the morning of June 24 measurements were made near the inlet of the liquid chemical scrubber at the end of a long section of straight ducting (2.5 to 3 m in length). The inside diameter of the flexible aluminum ducting was measured and found to be 14.6 cm (5.75 in.) which corresponds to an area of 167.5 cm<sup>2</sup> (0.180 ft<sup>2</sup>).

To measure air velocity, two four-point, equal-area traverses were made at points spaced 90° apart across the duct diameter. The air velocity measurement was then converted to a volumetric flow measurement. The result of this measurement (a flow rate of 1.97 m<sup>3</sup>/min) is shown in Table 1. From this measurement, and knowledge of the exact transit time of styrene-laden air through the liquid chemical scrubber (from inspection of the THC analyzer output recorded at the inlet and outlet of the pilot-scale scrubber), it was possible to accurately determine the total air flow rate into the pilot-scale scrubber during each period of testing. More information on these measurements is presented in Section 3.4 of this report.
#### **SECTION 3**

# DATA, RESULTS, AND DISCUSSION

### 3.1 TOTAL HYDROCARBON ANALYZER DATA

The THC's were operated continuously through the three days of testing. No operational problems were encountered with the THC monitors other than an infrequent flame-out of one of the FID's and occasional losses of power due to circuit breaker overload or accidental disconnection of power by plant personnel. Because these periods were short and because the instruments were monitored closely, no significant data were lost.

#### 3.1.1 Inlet Data

VOC emissions from the spraying process can be characterized as being quite variable. At the inlet of the pilot-scale liquid chemical scrubber instantaneous hydrocarbon emissions (essentially 100% styrene) ranged from as low as 50 ppm to as high as 250 ppm during spraying in the gelcoat booth. While molds were being removed from the spray booth or installed in the spray booth hydrocarbon emission levels ranged from 12 to 25 ppm. During midday lunch breaks in the production process, hydrocarbon levels decreased to approximately 5 ppm.

Figures 7 through 15 show output from the inlet THC analyzer that was recorded on the datalogger for the three days of testing, June 22 through 24, 1993. THC data taken during periods of calibration are not shown. For comparison purposes, data from the outlet THC analyzer are also shown on these figures. Outlet data will be discussed in Section 3.1.2, below.

These figures show that there are three distinct "periods" of spraying per day. The first period lasts from the start of spraying in the morning (from as early as 0700) and ends when the plant employees have a 15 minute break at approximately 1000 hours. The second period starts at approximately 1015 and lasts until the lunch break at noon. The final period starts around 1230 and lasts until approximately 1400. Spraying can end earlier than 1400 if daily production guotas are met.

These figures show the variability and the periodic nature of the emissions from this process. Because of the variety of molds (with different surface areas) that are sprayed and because of the



Time of Day, June 22, 1993

Figure 7. Inlet and outlet hydrocarbon emissions, 0830 to 1015, June 22, 1993

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Time of Day, June 22, 1993

Figure 8. Inlet and outlet hydrocarbon emissions, 1015 to 1200, June 22, 1993



Time of Day, June 22, 1993

Figure 9. Inlet and outlet hydrocarbon emissions, 1230 to 1400, June 22, 1993



Time of Day, June 23, 1993

Figure 10. Inlet and outlet hydrocarbon emissions, 0700 to 1030, June 23, 1993



Time of Day, June 23, 1993

Figure 11. Inlet and outlet hydrocarbon emissions, 1030 to 1215, June 23, 1993

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Time of Day, June 23, 1993

Figure 12. Inlet and outlet hydrocarbon emissions, 1230 to 1415, June 23, 1993



Time of Day, June 24, 1993

Figure 13. Inlet and outlet hydrocarbon emissions, 0730 to 1030, June 24, 1993

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Time of Day, June 24, 1993

Figure 14. Inlet and outlet hydrocarbon emissions, 1030 to 1215, June 24, 1993



Time of Day, June 24, 1993

Figure 15. Inlet and outlet hydrocarbon emissions, 1230 to 1400, June 24, 1993

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nature of the spraying process, it is difficult to determine if differences from one spraying period to another are due to differences in the type of mold (bath tub versus shower stall) or to the approach used by the operator. Because the periodic nature of these emissions have been observed in the past,<sup>3</sup> spraying activity in gel coat booth #2 was recorded on a video camera and the surface area of each mold was determined so that it would be possible to determine the level of styrene emissions as a function of the surface area sprayed.

#### 3.1.2 Outlet Data

Figures 7 through 15 also show output from the outlet THC analyzer that was recorded on the datalogger for the three days of testing, June 22 through 24, 1993. These data have been shifted to align with the inlet data. The amount of time that the data were shifted so that inlet and outlet peaks in styrene concentration align is equal to the transit time through the device. Transit times ranged from 1.70 minutes to 2.08 minutes. As with THC data from the inlet, periods of calibration are not shown. Also not shown are data from most periods when water was emptied from the outlet sampling line or when an FID flame-out occurred.

These data show that outlet emissions from the pilot scale liquid scrubber are closely coupled to inlet emissions. This behavior should be expected because of the relatively constant transit time for emissions to pass through the device. Thus, outlet emissions rose and fell with inlet emissions. Generally, peak outlet emissions ranged between 50 and 100 ppm (depending on the test condition) and between sprayings usually fell to levels equal to those measured at the inlet to the device at such times (5 to 30 ppm).

#### 3.1.3 Efficiency Data

During each period of spraying, styrene removal efficiency was determined by comparing average inlet and outlet THC measurements recorded by the dedicated PC-based data logger. In order to isolate periods of spraying activity in gel coat booth #2 from periods when no spraying was taking place in that booth, data were segregated into periods of time when inlet hydrocarbon emissions were greater than 30 ppm (which coincided with spraying) and periods when hydrocarbon emissions were equal to or lower than 30 ppm (which coincided with periods between spraying). 30 ppm was selected as a break point

from inspection of the data. After this segregation was made, outlet data (shifted to remove the effect of transit time through the pilot-scale scrubber, as shown in Figures 7 through 15) were averaged over the same time periods used for the inlet data and these averages were used to determine hydrocarbon (as styrene) removal efficiency for each mold that was sprayed. The results of these calculations are presented in Tables 5 through 7. These tables present average inlet and outlet THC emissions data and hydrocarbon removal efficiency averaged over each period of mold spraying and each test condition. Figures 16 through 18 present the efficiency averages from Tables 5 through 7 in the form of bar graphs showing hydrocarbon removal efficiency for each period of mold spraying (as individual bars) and for test condition (as thick horizontal lines over the time period of the test condition).

Raw averages of inlet and outlet THC data for periods during which inlet emissions were greater than 30 ppm and for periods when inlet emissions were less than or equal to 30 ppm are shown in Appendix C. These data were used to generate the results shown in Tables 5 through 7. In this appendix, population standard deviations and 95% confidence intervals are also included for each average. Because the inlet THC data were analyzed to determine periods during which hydrocarbon emissions were greater or less than 30 ppm, no attempt was made in Appendix C to segregate the results into groups corresponding to the test conditions shown in Tables 2 through 4. Therefore, the tables presented in Appendix C are organized by spraying periods (three per day).

These figures also show that the liquid chemical scrubber was not able to exceed an average hydrocarbon removal efficiency of greater than 55% for any of the 25 test conditions. When water was sprayed (only in reaction chamber 1), in the absence of any other chemical, the hydrocarbon removal efficiency averaged 33% (Test Condition 1 on 6/22). Indeed, when the liquid chemical scrubber was off line because of a water line rupture (with flow still maintained through the device), a hydrocarbon removal efficiency of 30% was measured! Thus, the greatest effect of any chemical additive was to increase average hydrocarbon removal efficiency by 26% over that obtained with water or 29% over that obtained by using the liquid chemical scrubber as a settling chamber.

Test			Mold		- Inlet Styr	rene Leve			Outlet Sty	rene Levi	el la	Average Efficiency		
Cond.	Mold	Moid	Spray	For Ea	ch Mold	Test C	ondition	For Ea	ich Mold	Test C	ondition	Per	Test C	ondition
#	#	Area	Time	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Mold	Average	Std. Dev.
		(m²)	(sec)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(%)	(%)	(%)
1	1	7.80	260	103.0	37.0	[		66.8	12.5			35.1		
	2	6.13	344	93.8	41.8	}		63.3	16.0			32.5		
	3	7.80	409	85.8	43.7			59.6	19.5			30.5	]	
	4	5.30	262	89.7	44.9	92.3	42.2	58.6	13.3	61.9	16.1	34.6	32.8	2.1
2	5	5.85	482	68.7	43.5			47.9	15.5			30.3		
	6	7.99	313	103.7	38.0	82.5	41.5	64.9	12.7	54.6	14.4	37.4	33.1	5.0
3	7	7.99	680	69.8	28.6			47.7	11.4			31.6		
	8	7.80	543	85.1	29.8			54.0	11.9			36.6		
	9	5.85	285	99.7	51.4	80.9	34.5	60.4	13.3	52.3	12.0	39.4	34.9	4.0
4	10	6 13	354	113.3	48.0	} :		85.9	20.0			24.1		
	11	5.30	272	106.8	54.4			67.6	18.7			36.7		
	12	7.80	520	102.7	46.3			71.2	18.8			30.6		
	13	1.39	385	77.5	49.3	99.5	49.0	54.4	14.5	69.7	18.1	29.8	30.0	5.2
5	14	7,99	434	106.7	49.5	ļ		71.3	17.5			33.2		
	15	7.80	303	123.9	53.1			78.4	17.3			36.8		
	16	7.99	511	103.7	54.6			65.7	21.9			36.7		
	17	7.80	464	101.1	52.4	107.4	52.5	63.3	21.0	68.7	19.8	37.4	36.0	1.9
6	18	5.30	197	100.9	39.6	100.9	N/A	49.4	7.6	49.4	N/A	51.1	51.1	N/A
7	19	7 99	357	126.4	43.8	[		71.7	14.7			43.3		
	20	5 30	261	107.1	42.4	118.2	43.2	60.8	11.3	67.1	13.4	43.2	43.3	0.1
8	21	5.30	302	100.7	51.2			59.7	13.2			40.8		
Ĭ	22	7 80	345	113.9	46.4	107.8	48.7	62.8	14.2	61.4	13.7	44.8	42.9	2.9
9	23	5.85	212	1127	49.3			49.5	10.8			56.1		
ľ	24	7.99	314	112.2	34.4	112.4	41.0	78.5	13.5	66.8	12.5	30.0	40.5	18.4

 
 Table 5.
 Inlet and Outlet Styrene Level and Efficiency of Styrene Removal for each Mold Sprayed and for each Test Condition, June 22, 1993.

Test			Mold		Iniet Styrene Level				Outlet Sty	rene Leve	el le	Average Efficiency		
Cond.	Mold	Mold	Spray	For Ea	ch Mold	Test C	ondition	For Ea	ch Mold	Test C	ondition	Per	Test C	ondition
#	#	Area	Time	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Mold	Average	Std. Dev.
		(m²)	(sec)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(%)	(%)	(%)
1	1	7.80	393	74.8	33.3	74.8	N/A	41.4	10.9	41.4	N/A	44.7	44.7	N/A
2	2	5.30	207	81.6	30,1			33.6	5.8			58.8		
	3	6.69	315	82.8	31.5	82.3	31.0	40.3	8.4	37.7	7.5	51.3	54.3	5.3
3	4	7.80	386	80.8	31.7			39.9	9.4			50.6		
	5	7.80	562	72.0	32.1	75.6	31.9	38.4	11.0	39.0	10.4	46.7	48.3	2.8
4	6	7.25	540	72.2	35.9			37.8	12.3			47.6		
	7	5.30	238	86.1	32.7			41.6	6.1			51.7		
	8	7.80	404	83.3	36.1	78.8	35.3	44.4	9.6	40.8	10.4	46.7	48.1	2.7
5	9	7.80	548	77.5	34.3			40.2	12.6			48.1		
1	10	5.85	426	72.0	36.5			37.9	8.9			47.3		
]	11	5.30	317	87.4	41.5			45.3	10.4			48.2		
	12	7 80	431	86.4	33.6	80.2	36.1	42.9	10.9	41.2	10.9	50.3	48.5	1.3
6	13	7.80	402	109.9	39.1	109.9	N/A	55.0	11.2	<b>5</b> 5.0	N/A	50.0	50.0	N/A
7	14	5.30	322	86.9	41.4	86.9	N/A	41.0	9.3	41.0	N/A	52.8	52.8	N/A
8	15	7 80	550	91.1	51.2			53.0	17.5			41.8	]	
1	16	7.80	469	99.9	42.9	95.1	47.5	59.3	14.7	55.9	16.3	40.6	41.2	0.8
9	17	5.30	269	106.7	45 8			55.7	10.0			47.8		
1	18	7.99	438	110.4	46.2	109.0	46.0	63.0	15.3	60.2	13.6	42.9	44.8	3.5
10	19	7.99	760	80.1	42.5			46.8	18.0			41.6		
	20	7 99	592	96.9	46.5			56.6	19.5			41.6		
l	21	5.85	315	110.6	43.3	91.8	44.1	60.6	13.2	52.9	17.7	45.2	42.3	2.1
11	22	7.99	719	85 4	50.8	85.4	N/A	49.9	20.0	49.9	N/A	41.5	41.5	N/A
12	23	7.99	374	100.4	36.2			52.9	13.5			47.4		
]	24	5 30	289	86.5	38.1			47.0	9.3			45.7		
	25	6.69	277	104.3	32.6	97.3	35.8	52.9	9.5	51.1	11.2	49.3	47.4	1.8
13	26	1.11	185	58.5	26.1			25.5	3.1			56.4		
	27	7.80	318	105.2	33.6			47.1	9.5			55.3		
	28	6.69	260	153.6	50.6			71.0	10.4			53.8		
1	29	7.80	262	109.0	41.7			48.7	11.0			55.3		
	30	5.67	331	93.0	41.3	105.9	40.0	44.1	7.9	48.3	9.0	52.6	54.5	1.5

Table 6.Inlet and Outlet Styrene Level and Efficiency of Styrene Removal<br/>for each Mold Sprayed and for each Test Condition, June 23, 1993.

Test			Mold	Inlet Styrene Level					Outlet Sty	rene Leve	el le	Ave	rage Efficiency —		
Cond.	Mold	Mold	Spray	For Ea	ch Mold	Test C	ondition	For Ea	ch Mold	Test C	ondition	Per	Test C	ondition	
#	#	Area	Time	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Mold	Average	Std. Dev.	
1		(m²)	(sec)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(%)	(%)	(%)	
1	1	7.99	371	85.7	27.8			47.8	9.8			44.3			
	2	7.99	437	87.8	32.9	86.8	30.7	49.4	12.4	48.6	11.3	43.7	<b>4</b> 4.0	0.4	
2	3	5.85	244	91.2	34.9			43.5	8.5			52.3			
	4	6.13	334	91.7	39.9			56.8	24.1			38.0			
	5	6.13	341	<b>95</b> .0	43.2	92.8	39.9	77.7	9.2	61.1	16.2	18.1	34.4	17.1	
3	6	5.85	263	92.2	40.9			68.4	7.1			25.8			
	7	7.99	387	103.2	44.8			67.8	14.4			34.3			
	8	7.80	374	91.5	39.6			56.7	11.0			38.0			
	9	7.25	331	114.2	47.2			64.0	10.6			44.0			
	10	7.99	492	97.1	44.2			59.3	15.4			38.9			
	11	7.99	295	104.1	42.8			63.0	13.3			39.5			
	12	7.99	500	83.8	32.5			51.6	6.4			38.4			
	13	6.69	435	87.6	41.6			55.0	14.1			37.2			
	14	5.85	312	104.3	46.9			55.2	13.5			47.1			
	15	7.99	519	97.6	59 0			58.7	22.4			39.9			
	16	7.80	439	125.0	61.7			71.3	20.0			43.0			
	17	7.99	359	131.9	58.1			71.6	18.4			45.7			
]	18	5 30	364	104.3	58.4			54.4	15.0			47.8			
	19	3.25	350	96.0	63.2			49.6	10.7			48.4			
	20	2.23	165	88.8	48 0			39.1	4.9			56.0			
	21	7.80	444	123.6	61.6			62.2	17.5			49.6			
	22	7.99	578	818	37.5			40.6	23.6			50.4			
	23	5.30	211	117.0	55.9			56.2	12.5			52.0			
	24	7.80	304	132.4	60.2			68.4	14.4			48.3			
	25	7.80	299	129.4	52.8			64.9	12.7			49.8			
	26	5.85	274	109.1	51.5			55.1	6.8			49 4			
	27	6.69	298	114.8	49.6			60.5	10.7			47.3			
	28	5.30	113	122.8	<b>38</b> .9	104.9	50.2	51.2	3.2	58.5	15.1	58.3	43.8	7.4	

 
 Table 7.
 Inlet and Outlet Styrene Level and Efficiency of Styrene Removal for each Mold Sprayed and for each Test Condition, June 24, 1993.



Figure 16. Hydrocarbon removal efficiency, June 22, 1993.

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Figure 17. Hydrocarbon removal efficiency, June 23, 1993

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Figure 18. Hydrocarbon removal efficiency, June 24, 1993

As indicated above, a wide variety of chemical additives and surfactants were tested. While the reasons for the choice of these exact chemicals has not been addressed in any literature supplied by the scrubber manufacturer, before the test, the manufacturer indicated that solutions of both sodium hypochlorite and sodium hydroxide (along with a surfactant to aid in dispersion) would be evaluated for styrene removal. It is reasonable to expect that a bleach would react with styrene to break it down into benzoic acid. Why the other chemicals were evaluated has not been addressed by the manufacturer.

## 3.1.4 Estimated Styrene Emissions from Gel Coat Booth #2

It is possible to estimate styrene emissions to the atmosphere from the shower stall and bath tub gel coating process from THC data taken at the inlet of the liquid chemical scrubber device. Using the methodology described above, THC data from each day of testing were inspected to determine times during which bath tubs or shower stall molds were sprayed. VOC emissions (assumed to be 100% styrene) were averaged over the time required to spray each bath tub or shower stall mold and multiplied by the time required to spray the mold to determine the emissions rate in milligrams of styrene per cubic meter per second of air flow. This value was multiplied by the flow rate of the gelcoat booth exhaust fan to obtain a mass emissions rate of styrene to the atmosphere for each bath tub or shower stall. The air flow through the outlet stack on gel coat booth #2 was measured to be 6.23 m<sup>3</sup>/s (dry, or 13,193 dscfm) on 6/17/93 as part of Phase 1 of this Work Assignment. Tables 8 and 9 shows the results of these calculations.

Table 8 summarizes hydrocarbon emissions during periods of mold spraying. Over the three days of testing sufficient data were acquired to estimate styrene mass emissions for a total of 82 separate mold sprayings. On the average,  $6.2 \pm 2.1$  minutes were required to spray a mold and during that time approximately 0.144 ± 0.043 kg of styrene per square meter of mold surface was vented to the atmosphere, assuming that the average flow rate of the exhaust fan in gel coat booth #2 equaled the flow rate measured on 6/17/93. In terms of emissions per mold, the 82 molds sprayed represented  $552.2 \text{ m}^2$  (5944 ft<sup>2</sup>) of mold area or an average of 6.73 m<sup>2</sup> (72.5 ft<sup>2</sup>) per mold. Thus, *during spraying*, approximately 0.97 ± 0.29 kg of styrene were emitted to the atmosphere for every mold that was sprayed. The fairly high standard deviations for these numbers are most likely due to the fact that many

Date	Start	End	Molds	Mold	-Sprav	Time		- Styrene	Emission	s
	Time	Time	Sprayed	Area	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
				(m <sup>2</sup> )	(sec)	(sec)	(kg/moid)	(kg/mold)	(kg/m <sup>2</sup> )	(kg/m <sup>2</sup> )
6/22/93	0834:55	1002:01	9	62.5	397.6	145.0	0.914	0.220	0.132	0.032
	1032:46	1155:11	8	52.2	405.4	92.5	1.133	0.256	0.174	0.039
	1239:47	1356:15	7	45.5	284.0	62.7	0.854	0.238	0.131	0.037
	Daily S	l ummary	24	160.3	396.7	118.0	0.970	0.257	0.145	0.038
6/23/93	0712:14	0955:17	13	90.3	397.6	110.7	0.870	0.224	0.125	0.032
	1031:03	1203:07	8	<b>5</b> 6.0	464.5	165.7	1.197	0.338	0.171	0.048
	1242:07	1403:20	9	57.0	335.0	153.4	0.888	0.366	0.140	0.058
	Daily S	 ummary 	30	203.4	351.2	143.7	0.962	0.326	0.142	0.048
6/24/02	0742:40	1000-30	12	92.6	360.5	80.3	0 033	0 190	0 130	0.026
0/24/93	1034:35	1206:00		56.2	302.2	121.0	1 120	0.355	0.179	0.057
	1244:16	1353:56	6	38.7	249.8	75.5	0.816	0.266	0.126	0.041
	Daily S	ummary	28	188.6	351.2	106.2	0.968	0.282	0.144	0.042
June 22-24	Test Su	immary	82	552.2	372.5	124.4	0.966	0.289	0.144	0.043

Table 8. Hydrocarbon Emissions from Direct Spraying in Gel Coat Booth #2, THC Data

Table 9. Total Hydrocarbon Emissions from Gel Coat Booth #2, THC Data

Date	Start	End	Molds	Mold	Time		- Styrene Er	nissions —	
	Time	Time	Sprayed	Area	Period	Average	Std. Dev.	Average	Std. Dev.
		_		(m²)	(hours)	(kg/mold)	(kg/mold)	$(kg/m^2)$	(kg/m <sup>2</sup> )
6/22/93	0834:55	1002:01	9	62.5	1.45	1.029	0.703	0.148	0.101
	1032:46	1155:11	8	52.2	1.37	1.250	0.970	0.192	0.149
	1239:47	1356:15	7	45.5	1.27	1.043	0.970	0.160	0.149
	Daily S	l ummary I	24	160.3	4.10	1.107	0.101	0.166	0.018
							0.055	0.457	0.400
6/23/93	0712:14	0955:17	13	90.3	2.72	1.091	0.855	0.157	0.123
	1031:03	1203:07	8	56.0	1.53	1.328	0.975	0.190	0.139
	1242:07	1403:20	9	57.0	1.35	1.018	0.766	0.161	0.121
	Daily S	l ummary 	30	203.4	5.61	1.132	0.132	0.167	0.015
6/04/02	0742-40	1000-30	13	93.6	2 30	1.054	0 843	0 146	0 117
0/24/93	1024-25	1206:00	0	56.2	1.52	1.004	1.005	0 201	0 161
	1244:16	1353:56	6	38.7	1,16	1.024	1.121	0.159	0.174
	Daily Si	l ummary I	28	188.6	4.98	1.112	0.102	0.165	0.023
June 22-24	Test Su	i J <b>mmary</b> 	82	552.2	14.69	1.118	0.114	0.166	0.019

different types molds were sprayed and that bath tub enclosures require a longer time to spray (with higher emissions) than smaller shower stalls.

It should be emphasized that the above numbers are strictly for periods of spraying (hydrocarbon emissions greater than 30 ppm). Overall emissions are somewhat higher than shown in Table 8 because during any given period, total emissions to the atmosphere, through gel coat booth #2, are a sum of the emissions that occur during the spraying of a mold and the emissions swept into the booth between sprayings. Emissions not directly associated with spraying can come from molds that have been sprayed and not yet removed from the booth, coated molds that are left outside the mouth of the booth while an adjacent booth is being cleared, or from recently sprayed molds passing in front of the booth. Total hydrocarbon emissions are shown in Table 9. Thus, for the three days of testing, *total* emissions averaged approximately  $0.17 \pm 0.02$  kg of styrene for every square meter of mold that was sprayed. Likewise, for every mold that was sprayed, the total emissions of styrene to the atmosphere averaged  $1.12 \pm 0.11$  kg of styrene. Comparing the emissions directly associated with spraying to total emissions, it appears that, on the average, approximately 13% of all the emissions are not directly associated with spraying.

#### 3.2 EPA METHOD 18 DATA

EPA Method 18, Adsorption Tube Procedure, was followed to obtain charcoal tube samples at the inlet and outlet of the liquid chemical scrubber situated at gel coat booth #2. Due to the nature of the adsorption tube sampling procedure, the desire to sample process emissions over an extended period, and expected inlet and outlet hydrocarbon emissions levels, sample times of from one to one and one-half hours were planned. Unfortunately, because test conditions frequently lasted for short times as one or another scrubber additive was evaluated to improve scrubber performance it was only possible to complete two concurrent sampling runs at the inlet and outlet of the liquid chemical scrubber.

On June 22, a sample of the 39 ppm styrene calibration standard was taken with an adsorption tube and on June 23, a sample of the 2.2 ppm styrene calibration standard was taken with an adsorption tube. At the liquid chemical scrubber, concurrent inlet and outlet adsorption tube samples were obtained

on the last day of sampling, June 24, during test condition #3. One run was made in the morning (from 1052 to 1125) and the other run was made in the afternoon, from 1332 to 1351. During both of these runs three molds were sprayed. No sampling problems were encountered during any of these runs.

Table 10 shows the sample times and sampling parameters that were used to take these samples and Table 11 presents the results of these measurements. Also shown in this table are results of measurements recorded with the inlet and outlet THC monitors that were averaged over the time period during which the adsorption tube samples were obtained. Standard deviations are not shown for these THC measurements because, in this case, they would quantify the effect of concentration variations due to normal process changes (spray guns being cycled from off to on to off) over the time that the adsorption tube sample was obtained rather than provide an overall uncertainty in the average emissions level.

Date	Sample	Sample ID No.	Start Time	End Time	Sample Time (min)	Sample Flow Rate (liters/min)	Sample Volume (liters)
						<u></u>	
6/22/93	Midrange Calibration Standard	1	0900	1000	60	0.210	12.62
6/23/93	Low Range Calibration Standard	2	1035	1140	65	0.306	19.90
6/24/93	Inlet, Liquid Chemical Scrubber	3	1052	1125	33	0.198	6.35
	Outlet, Liquid Chemical Scrubber	4	1052	1125	33	0.481	15.54
	Inlet, Liquid Chemical Scrubber	5	1332	1351	19	0.174	3.30
	Outlet, Liquid Chemical Scrubber	6	1332	1351	19	0.507	9.64

 
 Table 10.
 Sampling Conditions for Adsorption Tube Measurements made at Eljer Plumbingware, June 22-24, 1993. EPA Method 18 Sampling

With the exception of the low range calibration standard, the results shown in Table 11 indicate that the Method 18 measurements are lower than concurrent measurements made with the THC analyzers. Percentage differences (difference divided by average expressed as a percent) for the four concentration determinations that could be compared to THC measurements ranged from approximately 13% to 15% below the THC averages with the afternoon scrubber inlet measurement approximately 22% below the averaged THC value. Only styrene was detected in the analyses of these samples.

Sample	Sample ID No.	Start Time	End Time	Styrene Co Method 18	ncentration From THC	Difference THC-Method 18	Efficiency Meth. 18/THC
				(ppm)	(ppm)	(%)	(%)
Midrange Calibration Standard	1	0900	1000	35.8	39.1*	8.8	
Low Range Calibration Standard	2	1035	1140	2.28	2.2*	-3.6	
Inlet, Liquid Chemical Scrubber	3	1052	1125	70.5	80.0	12.6	
Outlet, Liquid Chemical Scrubber	4	1052	1125	41.3	48.1	15.2	41.4 / 39.9
Inlet, Liquid Chemical Scrubber	5	1332	1351	76.2	94.7	21.7	
Outlet, Liquid Chemical Scrubber	6	1332	1351	42.5	49.3	14,8	44.4 / 47.9

### Table 11. Results of Adsorption Tube and THC Measurements made at Eljer Plumbingware, June 22-24, 1993. EPA Method 18 Sampling.

\* Concentration determined for styrene calibration standard.

With respect to styrene removal efficiency, both methods yielded efficiencies between 40 and 50%. There is no clear reason for the differences observed between the THC and Method measurements, and agreement to within ± 10% was expected (see Appendix B). The fact that the THC measurements were consistently greater than the EPA Method 18 measurements points to the need for a larger set of Method 18 samples so that a better comparison could be made.

## 3.3 ANALYSIS OF RECOVERED SCRUBBER LIQUID SAMPLES

All samples were taken at reaction chamber drains. Samples of spent scrubber liquid were obtained from the first two reaction chambers on June 23 (at 1340) and from all three reaction chambers on June 24 (at 1040). On June 23, only water was injected in the third reaction chamber so no liquid sample was taken. In addition, a sample of the process water used to dilute the chemicals used for scrubbing was obtained on June 24 (at 1015). All liquid samples were preserved in 250 ml glass sample bottles with Teflon-sealed caps. It was originally intended to obtain more scrubber liquid samples. Unfortunately, because so many test conditions were tried, it was difficult to isolate a set of operating conditions (where reasonable styrene removal was obtained) that persisted for a long enough period to obtain a set of scrubber samples that were not contaminated by additives from a previous test condition.

The samples were kept at room temperature, away from light until they could be brought back to SRI's Birmingham, Alabama laboratories for analysis. The samples were returned to SRI on June 27 and, according to standard operating procedure, were placed in refrigerated storage until they could be analyzed. The samples were analyzed on August 25 and 26 according to EPA SW-846 Method 8240 using a Hewlett-Packard Model 5890 Series II Gas Chromatograph with a Hewlett-Packard Model 5971A Mass Selective Detector. This analysis employs a purge and trap procedure, and scrubber liquid samples from June 23 (Reaction Chamber's #1 and #2) and June 24 (Reaction Chamber #1) contained enough of the surfactant that was added to improve droplet dispersion that the samples generated a vigorous foam when they were purged. This required that the samples be diluted to the point where the level of foaming did not affect the analysis. The effect of this dilution was to reduce the sample size from 5 ml to 0.01 ml to 0.05 ml, depending on the sample, which significantly increased the detection limit for semivolatile and volatile organic compounds present in these samples (see Appendix D).

Table 12 summarizes the test conditions under which the samples were obtained and Table 13 presents the results of the analyses carried out on these samples. As Table 12 shows, the same additive was used in Reaction Chamber #1 during both of the test conditions for which liquid samples were obtained. However, on June 24, the rate of addition of the scrubber additive (2% H<sub>2</sub>SO<sub>4</sub> and surfactant "E") was approximately 1.75 times that used on June 23. The same additives were not used in the other reaction chambers. On June 23, a 5.25% solution of NaClO was added to Reaction Chamber #2 and water alone was added to Reaction Chamber #3. On June 24, 3% H<sub>2</sub>O<sub>2</sub> was added to both Reaction Chamber #2 and #3.

As Table 13 shows, styrene was detected in only the sample from Reaction Chamber #1 on June 24. This is not surprising, because styrene present in the liquid sample would continue to react with scrubber additives (such as sodium hypochlorite) within the reaction chamber, in the chamber drain system, and possibly after the sample was acquired before it was analyzed. Also, Table 13 shows that in all but one of the scrubber liquid samples, acetone and chloroform were detected. The presence of chloroform in liquid collected from Reaction Chambers #1 and #2 at 13:40 on June 23 could be explained by the use of sodium hypochlorite in both of these chambers earlier in the day. Acetone was

probably not detected in the one sample (Reaction Chamber #1, 6/23) because this sample had to be heavily diluted (0.01 ml in water as opposed to a 5 ml sample with no water dilution) to reduce foaming caused by the surfactant present in the sample. The sample from Reaction Chamber #1 taken on June 24 also had to be diluted to reduce foaming from the surfactant, but by much less (0.05 ml in water to make a 5 ml sample). Less dilution along with the fact that the additive flow rate to Reaction Chamber #1 on June 24 was 1.75 times that used on June 23, makes it probable that more compounds would be detected in that sample (e.g. acetone, carbon disulfide, and unreacted styrene) than in the sample obtained on June 23.

Table 12. Summary of Test Conditions During Which Scrubber Liquid Samples were Taken

					Scrubber	Additio	n Rate	Scrubber	Additio	n Rate	Scrubber	Addition	n Rate
Date	Test Cond.	Start Time	End Time	Sample Time	Reaction Chamber #1	Additive (lph)	Water (lph)	Reaction Chamber #2	Additive (lph)	Water (lph)	Reaction Chamber #3	Additive (lph)	Water (lph)
6/23	13	1324	1403	1340	H <sub>2</sub> SO <sub>4</sub> (2%), Surfactant "E"	0.60	34.07	NaCIO (5.25%)	2.56	34.07	H₂O Only	0.00	34.07
6/24	3	837	1353	1040	H <sub>2</sub> SO <sub>4</sub> (2%), Surfactant "E"	1.05	34.07	H <sub>2</sub> O <sub>2</sub> ( <b>3%</b> )	1.70	34.07	H <sub>2</sub> O <sub>2</sub> (3%)	1.32	34.07

 Table 13.
 Results of Analyses Carried out on Scrubber Liquid Samples

 and a Process Water Sample

Date	Time	Origin	Compound	Concentration	Detection Limit
				(µg/l)	(µg/l)
6/23	1340	Reaction Chamber #1	Chloroform	23300	410
		Reaction Chamber #2	Acetone	709	364
			Chloroform	39400	41
6/24	1040	Reaction Chamber #1	Acetone	1910	728
	1		Carbon Disulfide	104	280*
			2-Butanone	53400	1460
			Chloroform	230	82
			Styrene	1022	141
		Reaction Chamber #2	Acetone	2440	7.28
	<b>.</b>		2-Butanone	367	14.6
			Chloroform	1.65	0.82
		Reaction Chamber #3	Acetone	7.41	7.28
			Chloroform	7.31	0.82
6/24	1015	Process Water	Chloroform	<b>5</b> 5	0.82
			Bromodichloromethane	12.2	2.37
	1		1	1	

\* Conservative estimate of detection limit based on previous measurements of similar water samples.

The presence of 2-butanone in the sample from Reaction Chamber #1 on 6/24 is explained because MEKP, the peroxide of 2-butanone, was used in this chamber earlier in the day. It is possible that residual MEKP remained in Reaction Chamber #1 and that it was present in the sample collected on that day. It could have hydrolized before or after collection.

# 3.4 Total Flow Rate Data

Following the methodology described in Section 2.5.4, air flow into the liquid chemical scrubber was measured on the morning of June 24 with a thermal anemometer that had been calibrated in a wind tunnel at SRI's Birmingham, Alabama facility. As was indicated earlier, because the flow rate was lower than initially expected flow could not be measured according to EPA Method 1A with a standard pitot probe. Method 1A indicates that the minimum number of traverse points for round ducts between 0.1 and 0.3 m diameter is 8, providing that there are no flow disturbances within 10 duct diameters upstream and 8 duct diameters downstream. These criteria were satisfied and 8 traverse points were used, four each on two diameters, 90° apart. Table 14 presents the results of these measurements. The flow measurements made on June 24 (at 0845) were the actual flows used for testing.

Date and Time	Traverse Point	Port A Traverse m/min	Port B Traverse m/min	Average Flow Rate* m <sup>3</sup> /min
6/24/93, 0845	1	109.7	108.2	
	2	121.9	128.0	
	З	123.4	125.0	
	4	106.7	115.8	
Average				1.966

Table 14. Flow Rate Measurements at the Inlet of the Liquid Chemical Scrubber

The duct diameter was 14.6 cm

As indicated above, because it was found that flow into the liquid chemical scrubber was too low to allow the use a standard pitot to measure flow rate, it was not possible to measure flow into the device until a thermal anemometer could be received late on June 23. To determine the flow rate through the liquid chemical scrubber for the two earlier days of testing, the value for flow rate determined on June 24 was scaled according to the ratio of the transit time measured through the scrubber on June 22 and 23 compared to that measured for June 24. This is because the coordinated THC measurements made at the inlet and outlet of the liquid chemical scrubber allowed the transit time of styrene-laden air through the device to be determined. Once the transit time was known, flow could be scaled relative to the transit time and flow rate measurement made on the morning of June 24.

### **SECTION 4**

#### SUMMARY AND CONCLUSIONS

The purpose of this study was to evaluate the liquid chemical scrubbing process for controlling styrene emissions at a representative fiberglass shower stall and bath tub manufacturing plant. This process was evaluated with the aid of a small, transportable pilot-scale liquid chemical scrubber unit supplied by the manufacturer of full-scale devices that utilize this technology. The evaluation was carried out from June 22-24, 1993 at the Eljer Plumbingware facility located in Wilson, NC.

The liquid chemical scrubbing process takes advantage of a patented absorption technique based on the mass transfer equation that provides enhanced chemical reactivity with an atomized mist. The manufacturer asserts that the mist provides a large surface area where gas-liquid phase reactions take place that result in the removal of gaseous contaminants.

The major components of the pilot-scale system tested in this study included the three-chamber scrubber equipped with three spray nozzles and separate chemical metering pumps for each chamber, internal ducting to allow the chambers to be connected in a variety of configurations, and a variable speed exhaust fan. The pilot-scale unit is mounted on a large trailer for ease of transport.

This is a once-through process. Thus, spent scrubber liquids were disposed of and were not regenerated. While no attempt was made to address issues associated with the disposal of spent scrubber liquids, the chemical analyses reported in Appendix C suggest that such disposal is straightforward.

The pilot-scale liquid chemical scrubber was not able to achieve styrene removal efficiencies greater than 55% over a period of mold spraying although a number of additives were tried (including sodium hypochlorite, ethylene glycol, sulfuric acid, methyl ethyl ketone peroxide, hydrogen peroxide, and water). In the three days of testing 25 separate test conditions were completed.

In addition to the evaluation of the liquid chemical scrubbing process, it was possible to quantify styrene emissions in the spray booth exhaust to which the pilot-scale device was connected. These measurements showed that styrene was the only volatile organic compound present in the spray booth

exhausts at this facility and that time-averaged concentrations of styrene ranged from 0.14 kg of styrene per square meter of mold sprayed (during periods of active mold spraying) to 0.17 kg of styrene per square meter of mold sprayed when all of the emissions entering the spray booth (over a day of spraying) were accounted for.

# 4.1 ECONOMICS

The liquid chemical scrubber manufacturer was asked to provide a quotation for a full-scale system suitable for the Eljer facility. That system is described in Table 15. For such a full-scale device the installed cost was quoted to be \$475,000 with an hourly operating cost of \$10.01. Assuming an average styrene inlet concentration of 110 ppm, as was used in the previous economic analysis of the Polyad<sup>®</sup> FB system,<sup>3</sup> a system flow rate of 145,000 scfm, and a 50% styrene removal efficiency, the total cost depreciated over a nine year lifetime is \$9.04/scfm or \$563/ton of styrene removed.

Table 15. Design and Cost Specification for a Full-Scale Liquid Chemical Scrubber

# DESIGN ASSUMPTIONS AND COSTS

Air Capacity Iniet Temperature	145,000 75	scfm °F
Total System Efficiency	50	%
Hours of Operation per Year	2000	bours
Period of Depreciation	9	vears
Cost of Operation	10.01	\$/hr
Cost of Electrical Power	0.07	\$/kWh
Sodium Hypochlorite	0.37	\$/ib (dry)
Surface Active Agent	10	\$/gallon
Installed Cost	475,000.00	\$
Total Cost	563.36	\$/ton of styrene removed (over 9 year life)
	9.04	\$/scfm (over 9 year life)

# LIQUID CHEMICAL SCRUBBER DESIGN

Layout		Horizontal
Inlet Duct		Openings into Plenum from Spraybooths
Exhaust	14 x 7	ft (into Horizontal Construction)
Stack Height	28	ft ,
Reaction Chamber		
Number	1	Chamber
Reaction Time	10	Seconds
Effective Chamber Volume	24,167	ft <sup>3</sup>
Dimensions 14 x 1	4 x 135	ft (with Plenum)
14 x	7 x 129	ft (Chamber without Plenum)
EXHAUST FAN		Existing
CHEMICAL SUPPLY SYSTEM		Single Stage / 2 Chemicals
LIQUID DISTRIBUTION SYSTEM		
Number of Nozzies	15	(Model No. Q-1)
Flow Rate	0.75	gal/min (per Nozzle)
	11.25	gal/min (Total)
Compressed Air		• • •
Flow Rate	60	scfm (per Nozzle)
	900	scfm (Total)
Pressure	80	psig
ELECTRICAL CONTROLS		Standard, per Local Code
ACCESSORY EQUIPMENT		Air Compressor, 180 hp

#### SECTION 5

#### REFERENCES

- Mist Scrubbing Technology developed by QUAD Technologies, Inc. for odor control at rendering plants, flavor houses, landfill gas, composting, and other municipal applications. Mist Scrubbing Technology is protected by several United States and foreign patents, and patent applications. Among these are patent numbers 4,125,589, 4,225,566, B1-4,238,461, 4,302,226, 4,308,040, 4,416,861, and 4,844,874. Other patent applications are pending. The chemistry of compost scrubbing is covered by U.S patent 4,994,245 for which QUAD has an exclusive license.
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# APPENDIX A

.

# NIOSH METHOD 1501

FORMULA: Table 1

H.W.: Table 1

#### HYDROCARBONS, AROMATIC

METHOD: 1501 ISSUED: 2/15/84

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OSHA, NIOSH, ACGIH: Table 2

PROPERTIES: Table 1

COMPOUNDS:benzenecumemea-methylstyrenestyrenevinyltoluene(Synonymsp-tert-butyltolueneethylbenzenenaphthalenetoluenexylenein Table 1)

SAMPLING	MEASUREMENT		
SAMPLER: SOLID SCRBENT TUBE (coconut shell charcoal, 100 mg/50 mg)	! !TECHNIQUE: GAS CHROMATOGRAPHY, FID ! !ANALYTES: hydrocarbons listed above		
FLOW RATE, VOLUME: Table 3	1 1DESORPTION: 1 mL CS <sub>2</sub> ; stand 30 min 4		
SHIPMENT: no special precautions	INJECTION VOLUME: 5 µL		
SAMPLE STABILITY: not determined	ITEMPERATURE-INJECTION: 225 °C -DETECTOR: 225 °C		
BLANKS: 2 to 10 field blanks per set	: -COLUMN: see step 11		
BULK SAMPLE: desirable, 1 to 10 mL; ship in separate containers from samples	CARRIER GAS: N <sub>2</sub> or He, 25 mL/min ! !COLUMN: glass, 3.0 m x 2 mm, 10% OV-275 on		
ACORACY	for equivalent		
RANGE STUDIED, BIAS and OVERALL PRECISION (s <sub>r</sub> ): Table 3	! !CALIBRATION: analytes in CS <sub>2</sub> ! !RANGE AND PRECISION (s <sub>r</sub> ): Table 4 ! !ESTIMATED LCD: 0.001 to 0.01 mg per sample ! with capillary column [1]		

APPLICABILITY: This method is for peak, ceiling and TWA determinations of aromatic hydrocarbons It may be used for simultaneous measurements, though there is the possibility that interactions between analytes may reduce the breakthrough volumes and change desorption efficiencies. INTERFERENCES: Use of the recommended column will prevent interference by alkanes ( $\leq C_{10}$ ). Under conditions of high humidity, the breakthrough volumes may be reduced by as much as 50%. Other volatile organic solvents, e.g., alcohols, ketones, ethers and halogenated hydrocarbons, are possible interferences. If interference is suspected, use a less polar column or change column temperature. OTHER METHODS: This method is based on and supercedes Methods P&CAM 127, benzene, styrene,

other METHODS: Into method is based on and supercedes methods FoCAH 121, benzene, styrene, toluene and xylene [2]; S311, benzene [4]; S22, <u>p-tert</u>-butyltoluene [3]; S23, cimene [3]; S29, ethylbenzene [3]; S25,  $\alpha$ -methylstyrene [3]; S292, naphthalene [4]; S30, styrene [3]; S343, toluene [4]; S25, vinvitoluene [3]; S318, xvlene [4].

#### REAGENTS:

- Eluent: Carbon disulfider, chromatographic quality containing (optional) suitable internal standard.
- 2. Analytes, reagent grade=
- 3. Nitrogen or helium, purified
- 4. Hydrogen, prepurified.
- 5. Air, filtered.
- Naphthalene calibration stock solution, 0.40 g/mL in CS<sub>2</sub>.

\*See Special Precautions.

EQUIPMENT:

- Sampler: glass tube, 7 cm long, 6 mm 00, 4 mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg, back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
- Personal sampling pumps, 0.01 to 1 L/min (Table 3), with flexible connecting tubing.
- 3. Gas chromatograph, FID, integrator, and column (page 1501-1).
- 4. Vials, glass, 1-mL, with PTFE-lined caps.
- 5. Piper, 1-mL, and pipet bulb.
- 6. Syringes, 5-, 10-, 25- and 100-uL.
- 7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and extremely flammable (flash point = -30 °C); benzene is a suspect carcinogen. Prepare samples and standards in a well-ventilated hood.

SAMPLING:

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

SAMPLE PREPARATION:

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

CALIBRATION AND QUALITY CONTROL:

- 8. Calibrate daily with at least five working standards over the appropriate range (ca. 0.01 to 10 mg analyte per sample; see Table 4).
  - a. Add known amounts of analyte (calibration stock solution for naphthalene) to eluent in 10-mL volumetric flasks and dilute to the mark.
  - b. Analyze together with samples and blanks (steps 11, 12 and 13).
  - c. Prepare calibration graph (peak area of analyte vs. mg analyte).

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- Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
  - a. Remove and discard back sorbent section of a media blank sampler.
  - b. Inject a known amount of analyte (calibration stock solution for naphthalene) directly onto front sorbent section with a microliter syringe.
  - c. Cap the tube. Allow to stand overnight.
  - d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11, 12 and 13).
  - e. Prepare a graph of DE vs. mg analyte recovered.
- 10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

HEASUREMENT :

 Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1501-1. Select appropriate column temperature:

	Approximate	Retention Time	(min), at Indicated	Column Temperature
Substancea	<u>50 °C</u>	<u>00 °C</u>	150 °C	Programmed
benzene	2.5			2.5
toluene	4.3	1.1		4.2
xylene (para)	7.0	1.4		5.2
ethylbenzene	7.0	1.4		5.5
xylene (meta)	7.2	1.5		5.6
cumene	8.3	1.6		6.0
xylene (orthc)	10	1.9		6.5
styrene	16	2.6		7.5
a-methylstyrene		3.2	1.0	8.1
vinyltoluene (meta)		3.8	1.2	8.5
naphthalene		25	4.3	12

<sup>a</sup>Data not available for <u>p-tert</u>-butyltoluene and <u>p-vinyltoluene</u>.

<sup>b</sup>Temperature program: 50 °C for 3 min, then 15 °C/min to 200 °C.

NOTE: Alternatively, column and temperature may be taken from Table 4.

12. Inject sample aliquot manually using solvent flush technique or with autosampler. NOTE: If peak area is above the linear range of the working standards, dilute with eluent,

reanalyze and apply the appropriate dilution factor in calculations.

13. Measure peak area.

CALCULATIONS:

14. Determine the mass, mg (corrected for DE) of analyte found in the sample front  $(W_{\rm f})$  and back  $(W_{\rm b})$  sorbent sections, and in the average media blank front  $(B_{\rm f})$  and back  $(B_{\rm b})$  sorbent sections.

NOTE: If  $W_{\rm b} > W_{\rm f}/10$ , report breakthrough and possible sample loss.

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15. Calculate concentration, C, of analyte in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

Precisions and biases listed in Table 3 were determined by analyzing generated atmospheres containing one-half, one, and two times the OSHA standard. Generated concentrations were independently verified. Breakthrough capacities were determined in dry air. Storage stability was not assessed. Measurement precisions given in Table 4 were determined by spiking sampling media with amounts corresponding to one-half, one, and two times the OSHA standard for nominal air volumes. Desorption efficiencies for spiked samplers containing only one compound exceeded 75%. Reference [12] provides more specific information.

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- HETHOD REVISED BY: R. Alan Lunsford, Ph.D., and Julie R. Okenfuss; based on results of NIOSH Contract CDC-99-74-45.

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#### HETHOD: 1501

Table 1. Synchyms, formula, molecular weight, properties [5].

		Emisian)	Molec-	Boiling	Vapor Pressure A 25 Pr		Density	
Name/Synchyms	Structure	Formula	Weight	(°C)	(mm Hg)	(kPa)	€ 20 °C (g/mL)	
benzene CAS #71-43-2	$\bigcirc$	ႺჅႹჇ	79.11	80.1	95.2	12.7	0.879	
g- <u>tert</u> -butyltoluene CAS #98-51-1 1- <u>tert</u> -butyl-4-methy	lbenzene	C11H16	148.25	192.8	0.7	0.09	0.961	
CLTERE CAS #98-82-3 isopropylbenzene	$\bigcirc \prec$	CgH12	120.20	152.4	4.7	0.62	0.862	
ethylbenzene CAS #100-41-4	$\bigcirc \neg$	C8H10	106.17	136.2	9.5	1.28	0.867	
ca-methylstyrene CAS #98-83-9 isopropenylbenzene (l-methylethenyl)-be	nzene	<b>с<sub>9</sub>н<sub>10</sub></b>	118.18	165.4	2.5	0.33	0.911	
naphthalene CAS #91-20-3	$\bigcirc \bigcirc$	с <sup>10</sup> н8	128.18	80.2 <sup>a</sup>	0.2	0.03	1.025	
styrene CAS #100-42-5 vinylbenzene	$\bigcirc \neg$	с <sup>8</sup> н8	104.15	145.2	6.1	0.81	0.906	
toluene CAS #108-88-3 methylbenzene	$\bigcirc$	с <sub>7</sub> н <sub>8</sub>	92, 14	110.6	28.4	3.79	0.867	
vinyltoluene <sup>b</sup> CAS #25013-15-4 methylstyrene (g methylvinylbenzene		دوبلا <sub>10</sub> ( <u>مع</u> (وي	118.18 <u>ta)</u> <u>ra)</u> tho)	167.7 171.6 172.8 169.8	1.6 1.9 1.8 1.8	0.22 0.26 0.24 0.24	0.898 0.911 0.911 0.904	
xylene <sup>c</sup> CAS #1330-20-7 dimethylbenzene	(g-xylene)	دو۲ <sub>10</sub> (مر روع روع	106.17 <u>tho</u> ) <u>ta</u> ) <u>ra</u> )	144.4 139.1 138.4	6.7 8.4 8.8	0.89 1.12 1.18	0.880 0.864 0.861	

Melting point. <sup>b</sup>Commercial mixture of <u>meta</u> and <u>para</u> isomers.

CHixture of isomers.

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		OSHA		NIC	5H		ACGI	+	mq/m <sup>3</sup>
Substance	THA	Ē	Peak	THA	<u>c</u>	TLV	STEL		per pom
benzene	10	25	50ª	1		10-	* 25;	irit	3.19
<u>p-tert-butyltoluene</u>	10					10	20		6.05
cumene	50	(skin)				50	75	(skin)	4.91
ethylbenzene	100					100	125		4.34
a-methylstyrene		100				50	100		4.83
naphthalene	10					10	15		5.24
styrene	100	200	600 <sup>b</sup>	50	100	50	100		4.26
toluene	200	300	5004	100	200*	100	150	(skin)	3.77
vinyltoluene	100					50	100		4.83
xylene	100			100	200*	100	150		4.34

Table 2. Permissible exposure limits, ppm [6-11].

Maximum duration 10 min in 8 hr. Maximum duration 5 min in any 3 hr. \*\*ACGIH: suspect carcinogen [10].

≠ 10-min sample.

Table 3.	Sampling flowrate <sup>a</sup> ,	volume,	capacity, range,	overall b	ias and	precision	[3,4,	12].
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	Sampling			<u>Break</u> Vol	une a	Range at	Overall		
	Flowrate	Volum	e (L)	Conce	ntration	VOL-NCH	Bias	Precision	
Substance	(1/min)		VOL-MAXD	<u>(L)</u>	(mg/m <sup>3</sup> )	(mg/m <sup>3</sup> )	(5)	(s <sub>r</sub> )	
benzene	≤0.20	2 <sup>c</sup>	30	>45	149	42- 165	0.8	0.059	
p-tert-butyltoluene	≨0.20	10	29	44	112	29- 119	-10.4	0.071d	
currene	≦0.20	10	30	>45	480	120- 480	4.6	0.059	
ethylbenzene	≨0.20	10	24	35	917	222 - 884	-8.1	0.089 <sup>d</sup>	
a-methylstyrene	<b>≨0.2</b> 0	3f	30	>45	940	236- 943	-10.8	0.061d	
naphthalene	≦1.0	200	200	>240	81	19- 83	-0.5	0.055	
styrene	≦1.0	59	14	21	1710	426-1710	-10.7	0.058 <sup>d</sup>	
toluene	≦0.20	2 <sup>C</sup>	8	12	2294	548-2190	3.8	0.052	
vinyltoluene	≦0.20	10	24	36	952	256- 970	-9.5	0.061d	
xylene	≦0.20	12	23	35	870	218- 870	-2.1	0.060	

<sup>a</sup>Minimum recommended flow is 0.01 L/min.

<sup>b</sup>Approximately two-thirds the breakthrough volume, except for naphthalene.

clo\_min sample.

dCorrected value, calculated from data in Reference 12.

Maphthalene shows poor desorption efficiency at low loading; 100-L minimum volume is recommended.

fl5-min sample.

95-min sample.

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	Desorption <u>Measurem</u>		enent	ment Carrier		Column Parameters <sup>D</sup>			
	Volume	Range	Precision	Flow	t	Length			
Substance	(mL)	(mg)	(s <sub>T</sub> )	(mL/min)	(°C)	(m)	PackingC		
benzene	1.0	0.09- 0.35	0.036	50	115	0.9	A		
<u>g-tert</u> -butyitoluene	0.5	0.27- 1.09	0.021d	50	115	3.0	8		
cunene	0.5	0.86- 3.46	0.010	50	<del>9</del> 9	3.0	8		
ethylbenzene	0.5	2.17- 8.67	0.010	50	85	3.0	8		
a-methylstyrene	0.5	0.69- 3.57	0.011	50	115	3.0	8		
naphthalene	1.0	4.96-19.7	0.019	30	125	3.0	C		
styrene	0.5	2.17- 8.49	0.013d	50	109	3.0	8		
toluene	1.0	1.13-4.51	0.011	50	155	0.9	D		
vinyltoluene	0.5	2.41- 9.54	0.008	50	120	3.0	B		
xylene	1.0	2.60-10.4	0.010	50	180	0.9	D		

Table 4. Measurement range, precision and conditions<sup>4</sup> [3,4,12].

<sup>a</sup>Injection volume, 5.0 µL; nitrogen carrier gas.

bAll columns stainless steel, 3.2 mm outside diameter.

CA, 50/80 mesh Porapak P; B, 10% FFAP on 80/100 mesh Chromosorb W Al-OMCS;

C, 10% OV-101 on 100/120 mesh Supelcoport; D, 50/80 mesh Porapak Q.

<sup>d</sup>Corrected value, calculated from data in [12].

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# APPENDIX B

## 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, certified calibration gases (nominal values of 5, 50, and 200 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 (NIOSH Method 1501) and THC sampling. Unfortunately, as documented below, the concentrations of the styrene calibration gases were incorrectly determined by the vendor, Matheson Gas Products, Inc. Actual concentrations were determined to be 2.2, 39.1, and 170.8 ppmv of styrene, respectively.

EPA personnel were on site to oversee diagnostic measurements. In the field, QC was addressed by strict adherence to standard sampling protocols either as specified for EPA Method 18 (NIOSH Method 1501) 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 SRI's Analytical Chemistry facilities, QC is addressed by strict adherence to standard operating procedures (SOP) previously defined and implemented. Pertinent SOP's for the analyses required on this project were included in the QAPP. 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.

For the most part, the data quality indicator (DQI) goals for this project were achieved. However, significant problems were encountered with the calibration gases purchased for this test and these problems could have compromised virtually all of the data. These difficulties are discussed below.

#### 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, 1993. 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 SRI was incorrect. Therefore, a two-pronged investigation followed that focused on the possibility that the styrene calibration gases were in error, that SRI 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 (used in Phase 2 of this Work Assignment as the calibration standard) 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 SRI.

With respect to SRI'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 EPA Method 18, 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 Elier 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 Mathesoncertified 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 SRI on September 17 and the results of SRI'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 SRI'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 B-1. Table B-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 B-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 ( $\leq$  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

Table B-1. Results of SRI 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 ± RSD	56.6 ± 1.5%	58.6 ± 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 ± 2.2% RSD.
- \*\* Analysis by EPA Method 18, Absorption Tube Procedure, with GC/FID. Aside from the diluent (CS<sub>2</sub>), styrene was the only material detected.

Matheson Analysis*	SRI Method 18 Analysis**		SRI THO	Analysis'	Comparability
(ppm)	(ppm)	RSD (%)	(ppm)	RSD (%)	(% 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

Table B-2. Results of SRI Analyses of Matheson Calibration Gas

\* 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 ± 0.24 ppm with propane-based calibration).

the Cylinder exhausted before THC measurements could be made.

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 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.

Correction of the THC data was straightforward. During the test, only the nominal 52 ppm styrene calibration gas (actually 39.1 ppm by later analysis) was used to calibrate the THC analyzers. Because the cylinder of this gas was emptied before the THC measurements reported in Table B-2 could be made, results obtained with these analyzers were scaled by a ratio of 0.7519 (or 39.1/52).

#### DATA QUALITY

The following procedures were used to determine how well data quality indicator (DQI) goals were met:

<u>Precision</u> 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 expresses as a difference or percent difference between measured and known values:

$$%$$
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.

 <u>Completeness</u> is expressed as a percent between successful analyses and total attempts:

Completeness =  $100 \times S/A$ 

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:

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

where R1 is the result for one method and R2 is the result for the second method.

Table B-3 shows the DQI goals that were estimated for critical measurements in the QAPP. Table B-4 shows DQI values for measurements carried out with charcoal tubes (EPA Method 18, Adsorption Tube Procedure, equivalent to NIOSH Method 1501) and Table B-5 shows DQI values for THC analyzer measurements. Below, the precision, accuracy, and completeness of the data that were obtained in this project are reviewed.

#### Precision

Precision could not be established for the EPA Method 18 (NIOSH Method 1501) field measurements because a sufficient number of measurements could not be made to define a standard deviation (due to the short duration of all but three of the test conditions and the time lost waiting for acceptable performance). With respect to measurements obtained with the THC analyzers, precision was determined by the repetitive sampling of calibration gases. Table B-5 shows that the precision obtained with these devices was generally well below the initial estimate of  $\pm$  10% listed in Table B-3.

Table B-3. Data Quality Indicator Goals for Critical Measurements Estimated in QAPP

Method and Reference	Measurement Parameter	Experimental Condition	Expected Precision (Rel. Std. Dev., %)	Expected Accuracy (% Bias)	Completeness (%)
NIOSH 1501	Styrene Content	<ol> <li>Inlet and Outlet of control device,</li> <li>Calibration gas samples.</li> </ol>	5. 8*	-10.7*	90
Total Hydrocarbon Analyzer with FID. **	Hydrocarbon compounds in air.	<ol> <li>Inlet and Outlet of control device,</li> <li>Calibration gas samples.</li> </ol>	± 10†	± 5'	90

\* Precision and bias for sampling with charcoal-filled adsorption tube.

\*\* J.U.M. Model VE-7 THC Analyzer.

\* Estimated values. Precision and bias will be determined for each instrument

Table B-4. Data Quality Indicator Values for EPA Method 18 (NIOSH Method 1501) Measurements Made at Eljer Plumbingware\*

Method and Reference	Measurement Parameter	Experimental Condition	Measured Value (ppm)	Accuracy (% Bias)	Completeness (%)
EPA 18	Styrene	39.1 ppm cal gas	35.8	- 8.4	33
or NIOSH 1501	Content	2.16 ppm cal gas	2.28	5.6	33

\* Precision undetermined. Single samples

# Table B-5. Data Quality Indicator Values for THC Analyzer Measurements Made at Eljer Plumbingware\*

## INLET THC ANALYZER

Cal Gas/% Bias	2.16 ppm Styrene Cal Gas	Bias	39.1 ppm Styrene Cal Gas	Bias	170.8 ppm Styrene Cal Gas	Bias
	(THC Value)	(%)	(THC Value)	(%)	(THC Value)	(%)
6/22/93	2.13	-1.3	37.46 .	-4.2	150.33	-12.0
			37.46 38.96	-4.2 -0,4		
6/23/93	2.11	-2.2	37.95 37.69	-3.0 -3.6	148.80	-12.9
6/24/93			38.63 39.24	-1.2 0.4		
Average	2.12	-1.7	37.28 38.08	-4.7 -2.6	149.56	-12.4
Precision (%CV)	0.7		2.0		0.7	

#### OUTLET THC ANALYZER

Cal Gas/% Bias	2.16 ppm Styrene Cal Gas	Bias	39.1 ppm Styrene Cal Gas	Bias	170.8 ppm Styrene Cal Gas	Bias
	(THC Value)	(%)	(THC Value)	(%)	(THC Value)	(%)
6/22/93	2.21	2.2	36,42	-6.9	151.76	-11.1
			36.42	-6.9		
			39.18	0.2		
			39.05	-0.1		
6/23/93	2.05		36.01		149.96	
			37.89			
6/24/93			37.08			
			37.26			
Average	2.13	2.2	37.41	-3.4	150.86	-11.1
Precision (%CV)	5.2		3.2	1	0.8	

\* Completeness was 99.6% for both THC analyzers.

#### <u>Bias</u>

For Method 18 each measurement of bias was less than the -10.7% DQI goal cited in Table B-3. Thus, this DQI goal was met, although only two samples were taken. For the THC analyzers, bias was determined for each measurement of the 2.16 and 170.8 ppm calibration gases and for the 39.1 ppm primary calibration gas before each calibration (before instrument span was set to 39.1 ppm). The DQI goal of  $\pm 5\%$  were easily met for the 2.16 and 39.1 ppm calibration gases but were not met for the 170.8 ppm calibration gas. 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 particular calibration gas. Completeness

For the NIOSH Method 1501 samples taken at the inlet and outlet of the Polyad FB device, completeness was 100% because every sample that was attempted was successfully analyzed.

For THC analyzer measurements, completeness was near 100%. Minuscule amounts of data were lost during FID flame-outs and some data was lost during a short power failure. Out of approximately 14.7 hours of data (at one data point per second) less than 3 minutes worth of data were lost due to FID flame-outs or power failures (completeness of 99.6%).

#### **Representativeness**

The design of the pilot-scale liquid chemical scrubber dictated much of the sampling strategy and sampling methodology practiced during this evaluation to obtain representative samples. The use of a large, flexible aluminum sampling line avoided contamination from plasticizers in a flexible plastic line. Location of the sampling line inlet (within the vent exhaust duct) and flow velocity into the Polyad FB unit (nominally 2 m/sec) assured that the sample extracted from the gel coat booth #2 exhaust was representative. Following the sample methodology recommended in Section 7.4 of EPA Method 18 (equivalent to NIOSH Method 1501) also assured that representative samples were obtained.

#### Comparability

The sampling plan for this project made provision for simultaneous sampling using the two measurement methods of this study which would allow comparison of the results when suitably averaged over the same sampling period. While fewer EPA Method 18 samples were obtained than were planned, two concurrent inlet outlet Method 18 runs were made that can be compared to THC measurements averaged over the time that the Method 18 samples were taken. Table B-6 shows this comparison.

Considering that the expected bias for the Method 18 measurements is - 10.7% and that the expected bias for the THC measurements was  $\pm$  5%, three of the four measurements lie within 15.7% of each other. The other measurement lies considerably outside of the acceptable range. These is no explanation for this difference, other than it would have been desirable to have had many more Method 18 samples to compare with concurrent THC measurements.

Sample	Start	End	Styrene Concentratio		Comparability
	Time	Time	Method 18	From THC	THC-Method 18
			(ppm)	(ppm)	(%)
Inlet, Liquid Chemical Scrubber	1052	1125	70.5	80.0	12.6
Outlet, Liquid Chemical Scrubber	1052	1125	41.3	48.1	15.2
Inlet, Liquid Chemical Scrubber	1332	1351	76.2	94.7	21.7
Outlet, Liquid Chemical Scrubber	1332	1351	42.5	49.3	14.8

Table B-6. Comparability of Method 18 and THC Analyzer Measurements

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APPENDIX C

TOTAL HYDROCARBON ANALYZER DAILY RESULTS

1	lune 2	2 1003	Flanead		ILET THE (DO	m)		THET THE (	00m)
	Ctart L	E. 1995	Time	Average		95% Cont	Average	Population	95% Coof
	Time	Time	(eeconde)	Average	Std Dov	interval		Std Dev	Interval
		11/110	ISUCONUS		SIG. Dav.	111001 V 2U		310. 044.	
	0000.00	0924:12	252	16 76	4.07	0.61	20.59	6 20	0.78
	0830 00	0034.12	253	67 67	9.37 22.76	736	39.20	5.23	178
	0034.13	0834.52		402.01	25.70	4.40	55.20	12 50	1 52
	0834.55	0039:14	200	103.01	30.90 6 20	0.60	21.57	7 25	0.79
	0639:15	0844:36	344	02.91	44.94	4.42	£1.07	15.04	170
	0844:37	0850:20	344	33.01	41.04	9.42	24.36	3.05	0.60
	0850:21	0853:07	10/	21.10	3.01	0.40	50.50	10.49	1.90
	0853:08	0859:56	409	00.70	43.07	4.23	26.56	0.12	0.14
	0859:57	0859:59	3	20.92	0.33	0.37	20.00	0.12	0.14
	0900:00	0900:07		32.07	1.10	0.77	20.00	7.30	1.03
	80:000	0903:25	198	10.09	3.03	0.51	21.00	1.37	1.00
	0903:26	0907:47	202	09.07	44.93	0.34	31.51	0.69	0.33
	0907:48	0908:03	16	20.00	0.03	0.31	31.51	0.00	0.33
	0908:04	0908:10		31.71	0.90	0.71	29.50	0.20	0.15
	0908:11	0908:14	4	29.40	0.22	0.21	29.22	0.11	0.17
	0908:15	0908:23	9	32.20	0.87	0.37	20.40	0.23	0.10
	0908:24	0908:27		23.71	0.20	0.20	21.00	0.14	0.14
	0908:29	0908:39	11	29.21	U.3/	3.90	47.97	0.20 15 AQ	1 30
	0908:40	0916:41	462	70.00	45.55	0.05	34.50	0.04	0.04
	0916:42	0916:46	5	29.30	0.31	0.21	33.00	1.50	0.32
	0916:47	0918:20	94	99.23	21.03	9.37	20.40	0.09	0.52
	0916.21	0918:23	3	23.92	0.09	0.10	23.43	0.05	0.10
	0918:24	0918:29	6	30.90	0.49	0.39	29.12	0.15	0.10
	0918:34	0918:36	3	29.53	0.44	0.50	20 31	0.00	0.00
	0918:38	0918:42	5	20.49	0.73	0.04	27.07	0.14	0.13
	0918:43	0918:48	6	31.70	1.19	0.95	27.35	3.20	0.12
	0918:49	0920:18	90	22,93	2.00	4.05	20.00	3.29	1.40
	0920:19	0925:31	313	103.70	30.04	4.21	40.73	0.44	0.30
	0925:33	0925:37	5	30.00	0.29	0.25	35.07	2.13	0.35
	0925:38	0926.08	31	24.01	2.20	0.79	33.97	2.13	0.75
	0926:09	0926:11	3	30.62	0.40	0.32	31 33	0.10	0.20
	0926:12	0926:14	3	29.58	0.35	0.39	30.45	0.15	0.14
	0926:17	0926:20	4	29.40	2.01	0.41	29.41	0.15	0.13
	0926:21	0926:38	18	32.73	2.01	0.33	20.41	3.57	0.30
	0926:39	0931-02	204	20.27	3.97	2.15	47.70	11 39	0.45
	0931:03	0942:22	680	30.74	20.39	2.15	28.00	0.05	0.00
	0942:25	0942:27	3	30.74	0.41	0.40	20.30	0.00	0.00
	0942:28	0942:30	3	29.28	0.42	0.40	28.70	0.02	0.02
	0942:35	0942:41		20.11	0.04	1.02	20.92	0.11	0.00
	0942:44	0943:10	21	23.33	£.03	4.40	20.02	1.40	0.00
	0943:11	0944 23	/3	41.3/	3.0/ 375	0.20	10 22	7.43	0.40
	0944:24	0947 39	190	17.01 B6.07	2.15	2 61	53 05	11 01	1 00
	094/:40	0056.40		20 30	0.45	0.33	38.95	0.47	0.35
	0950:43	0056.64		31 47	0.40	0.00	40.52	0.34	0.30
	0050:00	0050.54	5	20.15	0.35	0.44	41 84	0.28	0.27
	0056-50	00:000	4	32 30	1 29	0.05	43.88	0.20	043
	0057-07	00:7:00	10	27 22	1.30	0.95	47 47	125	0.77
	0057.47	1002.01	295	DO RR	51 41	5 07	60.35	13 31	1.55
	4000.00	1002:01	205	20.75	0.25	0.27	33 42	0.24	0.21
	1002:02	1002:00	5	31.03	0.20	0.20	31 00	0.53	0.31
	1002:07	1002:17		30.65	0.30	0.24	30.60	0.10	0.19
	1002:20	1002:23	4	20.00	0.27	0.24	20.53	0.13	0.23
	1002:24	1002.33		23.00	0.55	0.42	28.34	0.37	0.25
	1002:34	1002:42		27 65	1 14	0.40	25.00	0.30	0.35
	1002:43	1003/12	30	0.67	672	0.25	12 37	3.54	0.22
-	1003:15	1013:23	1005	9.01	5.12	0.00	12.01	<b></b>	J.22
1	Fasianian -		2997	82.02			54 27		
	Emissions	> 30 PPM	3007	20 10			24.03		
		< 30 PPM	1432	20.18			46 13		
	All	CHISSIONS	2319	00.00		L		لى	

Table C-1. THC Analyzer Results from June 22, 1993, First Period of Spraying

73.1% of time spent spraying, 0834 - 1003Outlier, from periods at the beginning and end of spraying.

June 2	2 1993	Flaosed	It	ILET THC (pp	m)	OL	TLET THC	
Start	End	Time	Average	Population	95% Conf.	Average	Population	95% Conf.
Time	Time	(seconds)		Std. Dev.	Interval		Std. Dev.	Interval
1020:00	1032:45	766	8.46	5.77	0.41	15.37	10.65	0.75
1032:46	1038:39	354	113.27	48.05	5.00	85.93	20.01	2.08
1038:40	1038.44	5	29.38	0.32	0.28	39.58	0.36	0.31
1038:46	1043:09	264	18.96	4.54	0.55	27.22	9.83	1.19
1043:10	1043:17	8	42.07	7.11	4.93	58.88	0.92	0.64
1043:18	1043:23	6	24.86	1.99	1.59	62.20	0.73	0.58
1043-24	1047:55	272	106.83	54.41	6.47	67.58	18.72	2.23
1047.56	1047-58	3	29.43	030	0.34	33.00	0.22	0.25
1047-59	1048:09	11	33 68	2 03	1.20	31.69	0.46	0.27
1048-10	1049-10	61	26.03	1 49	0.37	26.98	2.17	0.54
1049 11	1049 15	5	30.66	0.33	0.29	23.36	0.13	0.11
1049-16	1051-27	132	23.34	3.99	0.68	26.77	7.40	1.26
1051:28	1051:35	q	31.92	1 03	0.67	46.35	0.71	0.46
1051-37	1051-39	3	29.68	0.26	0.29	47.79	0.12	0.13
1051:40	1051-44	5	31.60	073	0.64	48.31	0.21	0.19
1051-45	1051-48	4	28 64	0.22	0.22	49 00	0,29	0.29
1051-49	1100.28	520	102 67	46 25	3,98	71.21	18.79	1.61
1100.20	1100-22	520	28.99	0.57	0.50	32.99	0.06	0.05
1100.23	1100.33	5	31.60	0.75	0.66	33 56	0.29	0.25
1100:34	1100.38	10	25.71	1 01	1 10	35.03	0.62	0.39
1100:39	1100.40	10	31 21	046	0.52	36 65	0.19	0.21
1100.49	1100.51	65	20.58	3.26	0.79	42 12	217	0.53
1100.52	1102.42	107	69.62	38.05	7.21	49.21	7.85	1 49
1101.57	1103.43	107	29.20	0.57	0.40	67.32	1 01	0 70
1103.44	1103.51	270	82.01	49.27	5.88	56.06	14.48	173
1103.52	1100 21	210	34.20	2.26	0.66	31 49	0.98	0.29
1100.23	1109.07	45	70.20	0.17	0.00	20.06	0.05	0.06
1109.06	1109-10	3	23.25	1.55	0.15	29.30	0.00	0.06
1109:11	1109.20	10	32.03	1.00	0.30	29.71	0.03	0.00
1109:21	1110:08	48	21.21	1.20	0.30	20.41	0.01	0.13
1110:11	1110:26	16	27.00	.1.01	0.79	20.00	0.24	0.12
1110:27	1110:47	21	39.07	0.00	2.00	20.71	0.33	0.14
1110:48	1110:53	6	29.08	0.57	0.40	24.57	0.10	0.00
1110:54	1110.56	3	30.79	0.34	0.39	24.12	6.63	0.04
1110:57	1117.28	392	10.00	4.01	0.40	19.55	0.03 E 47	0.00
1117:29	1119:39	131	20.71	37.05	0.40	<b>44</b> .34	0.47	0.54
1119:41	1119:44	4	30.71	0.38	0.30	59.90	0.43	0.42
1119:49	1119:52	4	29.37	0.20	0.20	65 74	0.59	0.30
1119:55	1119:58	4	29.73	0.08	0.00	00./1	17.54	0.40
1119:59	1124:49	291	122.90	49.40	3.00	03./3	17.34	2.01
1124:50	1130.11	322	10.9/	13.03	1.49	<b>∠1.</b> 4/ 78.20	20.00	4.20
1130:12	1135:19	303	123.95	53.08	5.90	10.39	17.27	1.94
1135:20	1135:49	30	20.11	1.0/	0.00	31.13	2.10	0.75
1135:50	1136:12	23	30.05	2.99	4.45	31.30	1.44	0.50
1136:13	1136:17	5	21.28	1.32	1.15	20.9/	0.21	0.10
1136:18	1136 24	7	30.47	3.8/	2.8/	25.00	0.28	0.21
1136:25	1136:57	33	27.42	1.33	0.45	25./9	0.82	0.28
1136:58	1137:03	6	32.17	1.15	0.92	25.24	0.14	0.11
1137:04	1138:13	70	25.10	2.10	0.49	34.62	6.42	1.50
1138:14	1146:44	511	103.73	54.63	4.74	65.69	21.85	1.89
1146:45	1147:27	43	18.12	6.34	1.90	42.34	4.79	1.43
1147:28	1155.11	464	101.12	52.44	4.77	63.31	21.04	1.91
1155:12	1100:12	301	16.56	3.24	0.37	11.32	8.75	0.99
1200:16	1200:19	4	43.19	8.05	7.89	0.57	0.00	0.00
1200:20	1216:03	791	0.72	1.37	0.10	5.87	12.99	0.91
Emissions	> 30 PPM	3404	100.43			67.40		
Emissions	< 30 PPM	1831	18.37			23.62		
All	Emissions	5235	71.73			52.09		

Table C-2. THC Analyzer Results from June 22, 1993, Second Period of Spraying

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65.0 % of time spent spraying, 1032 - 1200Outlier, from periods at the beginning and end of spraying.

Start Time         End Time         Time (seconds)         Average Std. Dev.         Population Interval         95% Conf. Interval         Average Std. Dev.         Population Interval         Population Std. Dev.           1222:40         1239:47         1239:46         1027         5.29         1.51         0.09         4.59         4.28           1239:47         1243:03         197         100.87         39.63         5.53         49.35         7.62           1243:04         1252:34         571         16.37         5.24         0.43         13.93         6.97           1252:35         1252:38         4         31.25         0.46         0.45         13.68         0.08           1252:39         1252:48         10         25.30         2.68         1.66         14.05         0.14           1252:30         1253:07         6         27.92         1.00         0.80         15.35         0.10           1253:08         1253:57         29         24.64         2.85         1.04         17.43         0.35           1254:00         1254:04         5         17.73         9.19         8.05         18.27         0.08           1254:05         1254:15         11	C (ppm)
Time         Time         (seconds)         Std. Dev.         Interval         Std. Dev.           1222:40         1239:46         1027         5.29         1.51         0.09         4.59         4.28           1239:47         1243:03         197         100.87         39.63         5.53         49.35         7.62           1243:04         1252:34         571         16.37         5.24         0.43         13.93         6.97           1252:35         1252:34         571         16.37         5.24         0.43         13.93         6.97           1252:39         1252:48         10         25.30         2.68         1.66         14.05         0.14           1252:39         1253:01         13         32.48         1.65         0.89         14.74         0.25           1253:02         1253:07         6         27.92         1.00         0.80         15.35         0.10           1253:08         1253:57         29         24.64         2.85         1.04         17.43         0.35           1254:00         1254:04         5         17.73         9.19         8.05         18.27         0.08           1254:05         1254:15	on 95% Conf.
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	/ Interval
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.26
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1.06
1252:35         1252:38         4         31.25         0.46         0.45         13.68         0.08           1252:39         1252:48         10         25.30         2.68         1.66         14.05         0.14           1252:39         1252:48         10         25.30         2.68         1.66         14.05         0.14           1252:49         1253:01         13         32.48         1.65         0.89         14.74         0.25           1253:02         1253:07         6         27.92         1.00         0.80         15.35         0.10           1253:08         1253:57         29         24.64         2.85         1.04         17.43         0.35           1254:00         1254:04         5         17.73         9.19         8.05         18.27         0.08           1254:05         1254:15         11         32.42         1.22         0.72         18.54         0.12           1254:05         1254:15         11         32.42         1.22         0.72         18.54         0.12           1254:16         1254:18         3         29.15         0.17         0.19         18.77         0.04           1255:14	0.57
1252:39         1252:48         10         25.30         2.68         1.66         14.05         0.14           1252:49         1253:01         13         32.48         1.65         0.89         14.74         0.25           1253:02         1253:07         6         27.92         1.00         0.80         15.35         0.10           1253:08         1253:28         21         31.96         1.63         0.70         16.13         0.35           1253:02         1253:57         29         24.64         2.85         1.04         17.43         0.35           1254:00         1254:04         5         17.73         9.19         8.05         18.27         0.08           1254:05         1254:15         11         32.42         1.22         0.72         18.54         0.12           1254:05         1254:15         11         32.42         1.22         0.72         18.54         0.12           1254:05         1254:15         11         32.42         1.22         0.72         18.54         0.12           1254:16         1255:13         55         35.65         2.49         0.66         18.94         0.08           1255:31	0.08
1252:49         1253:01         13         32.48         1.65         0.89         14.74         0.25           1253:02         1253:07         6         27.92         1.00         0.80         15.35         0.10           1253:08         1253:28         21         31.96         1.63         0.70         15.13         0.35           1253:09         1253:57         29         24.64         2.85         1.04         17.43         0.35           1254:00         1254:04         5         17.73         9.19         8.05         18.27         0.08           1254:05         1254:15         11         32.42         1.22         0.72         18.54         0.12           1254:05         1254:15         11         32.42         1.22         0.72         18.54         0.12           1254:16         1254:18         3         29.15         0.17         0.19         18.77         0.04           1255:14         1255:30         17         27.01         1.22         0.58         18.54         0.15           1255:31         1255:49         19         33.28         1.52         0.68         17.90         0.23           1255:31	0.09
1253:02         1253:07         6         27.92         1.00         0.80         15.35         0.10           1253:08         1253:28         21         31.96         1.63         0.70         16.13         0.35           1253:29         1253:57         29         24.64         2.85         1.04         17.43         0.35           1254:00         1254:04         5         17.73         9.19         8.05         18.27         0.08           1254:05         1254:15         11         32.42         1.22         0.72         18.54         0.12           1254:16         1254:15         3         29.15         0.17         0.19         18.77         0.04           1254:19         1255:13         55         35.65         2.49         0.66         18.94         0.08           1255:14         1255:30         17         77.01         1.22         0.58         18.54         0.15           1255:31         1255:49         19         33.28         1.52         0.68         17.90         0.23           1255:50         1256:30         41         21.60         3.18         0.97         16.78         0.46           1256:31	0.14
1253:08         1253:28         21         31.98         1.63         0.70         16.13         0.35           1253:29         1253:57         29         24.64         2.85         1.04         17.43         0.35           1254:00         1254:04         5         17.73         9.19         8.05         18.27         0.08           1254:05         1254:15         11         32.42         1.22         0.72         18.54         0.12           1254:16         1254:15         11         32.42         1.22         0.72         18.54         0.12           1254:16         1254:15         3         29.15         0.17         0.19         18.77         0.04           1254:19         1255:13         55         35.65         2.49         0.66         18.94         0.08           1255:14         1255:30         17         7.701         1.22         0.58         18.54         0.15           1255:31         1255:49         19         33.28         1.52         0.68         17.90         0.23           1255:50         1256:30         41         21.80         3.18         0.97         16.78         0.46           1256:31	0.08
1253:29         1253:57         29         24.64         2.85         1.04         17.43         0.35           1254:00         1254:04         5         17.73         9.19         8.05         18.27         0.08           1254:05         1254:15         11         32.42         1.22         0.72         18.54         0.12           1254:16         1254:15         11         32.42         1.22         0.72         18.54         0.12           1254:16         1254:18         3         29.15         0.17         0.19         18.77         0.04           1254:19         1255:13         55         35.65         2.49         0.66         18.94         0.08           1255:14         1255:30         17         27.01         1.22         0.58         18.54         0.15           1255:31         1255:49         19         33.28         1.52         0.68         17.90         0.23           1255:50         1256:30         41         21.80         3.18         0.97         16.78         0.46           1256:31         1256:33         3         31.48         0.49         0.55         15.91         0.02	0.15
1254:00         1254:04         5         17.73         9.19         8.05         18.27         0.08           1254:05         1254:15         11         32.42         1.22         0.72         18.54         0.12           1254:16         1254:15         11         32.42         1.22         0.72         18.54         0.12           1254:16         1254:18         3         29.15         0.17         0.19         18.77         0.04           1254:19         1255:13         55         35.65         2.49         0.66         18.94         0.08           1255:14         1255:30         17         27.01         1.22         0.58         18.54         0.15           1255:31         1255:49         19         32.28         1.52         0.68         17.90         0.23           1255:50         1256:30         41         21.80         3.18         0.97         16.78         0.46           1256:31         1256:33         3         31.48         0.49         0.55         15.91         0.02	0.13
1254:05         1254:15         11         32.42         1.22         0.72         18.54         0.12           1254:16         1254:18         3         29.15         0.17         0.19         18.77         0.04           1264:19         1255:13         55         35.65         2.49         0.66         18.94         0.08           1255:14         1255:30         17         27.01         1.22         0.58         18.54         0.15           1255:31         1255:49         19         33.28         1.52         0.66         17.90         0.23           1255:50         1256:30         41         21.60         3.18         0.97         16.78         0.46           1256:31         1256:33         3         31.48         0.49         0.55         15.91         0.02	0.07
1254:16         1254:18         3         29.15         0.17         0.19         18.77         0.04           1254:19         1255:13         55         35.65         2.49         0.66         18.94         0.08           1255:14         1255:30         17         27.01         1.22         0.58         18.54         0.15           1255:31         1255:49         19         33.28         1.52         0.68         17.90         0.23           1255:50         1256:30         41         21.80         3.18         0.97         16.78         0.46           1255:31         1256:33         3         31.48         0.49         0.55         15.91         0.02	0.07
1254:19         1255:13         55         35.65         2.49         0.66         18.94         0.08           1255:14         1255:30         17         27.01         1.22         0.58         18.54         0.15           1255:31         1255:49         19         33.28         1.52         0.68         17.90         0.23           1255:50         1256:30         41         21.80         3.18         0.97         16.78         0.46           1255:31         1256:33         3         31.48         0.49         0.55         15.91         0.02	0.04
1255:14         1255:30         17         27.01         1.22         0.58         18.54         0.15           1255:31         1255:49         19         33.28         1.52         0.68         17.90         0.23           1255:50         1256:30         41         21.80         3.18         0.97         16.78         0.46           1256:31         1256:33         3         31.48         0.49         0.55         15.91         0.02	0.02
1255:31         1255:49         19         33.28         1.52         0.68         17.90         0.23           1255:50         1256:30         41         21.80         3.18         0.97         16.78         0.46           1256:31         1256:33         3         31.48         0.49         0.55         15.91         0.02	0.07
1255:50 1256:30 41 21.80 3.18 0.97 16.78 0.46 1256:31 1256:33 3 31.48 0.49 0.55 15.91 0.02	0.10
	0.14
	0.02
1256:34 1259:47 194 19:18 1.88 0.26 19:58 7.31	1.03
1259:48 1305:44 357 126:35 43.84 4.55 71.65 14.65	1.52
1305:45 1308:30 166 22.21 3.23 0.49 35.00 0.55	1.00
1308:31 1312:51 261 107.15 42.39 5.14 60.65 11.34	1.30
1312:52 1313:22 31 27.26 1.72 0.61 34.37 1.46	0.51
1313:25 1313:51 27 28:97 0.08 0.20 32:42 0.72	0.27
1313:52 1318:53 302 100.74 51.19 5.77 59.08 13.23	1.43
1318:54 1320:54 121 22:94 2.01 0.36 20.39 5.21	0.93
1320:55 1321:03 9 34.02 1.69 1.23 10.95 0.21	0.14
1321:04 1322:44 101 22:08 2:34 0.46 22:28 4.32	0.64
1322:45 1328:29 345 113.89 40.42 4.90 02.04 14.19	1.50
1328:30 1330:58 149 17.49 4.72 0.76 23.57 7.07	0.00
	0.03
	0.50
	0.35
1338 15 1338 22 8 55.14 1.39 1.30 10.02 0.40	0.80
1330.23 1330.35 33 21.44 2.45 0.00 22.00 2.04	1.46
1330.30 1342.27 212 112.73 43.20 0.00 43.40 10.00	0.52
1251.02 1255.15 214 112.20 34.37 3.80 78.50 13.51	1.49
1001102 100010 514 112.20 54.01 5.00 10.00 10.00 10.00 10.00 10.00	1 66
1300.10 1307.27 72 20.07 2.20 0.02 0.00 7.19 1957.09 1957.00 2 31.41 0.14 0.16 44.77 0.20	0.23
1357.20 1357.30 3 51.41 0.14 0.10 4.17 0.20 1357.31 1405.00 460 314 452 0.43 21.95 716	0.66
1007.01 1405.00 400 0.14 4.02 0.40 21.50 7.10	
Emissions > 30 PPM 2139 106.07 60.19	
Emissions < 30 PPM 2519 18.13 20.23	
All Emissions 4658 58.51 38.58	

Table C-3. THC Analyzer Results from June 22, 1993, Third Period of Spraying

45.9% of time spent spraying, 1239 - 1357 • Outlier, from periods at the beginning and end of spraying.

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June 2	3, 1993	Elapsed		ILET THE (DD	m)	01	TLET THC (	ppm)
Start	End	Time	Average	Population	95% Conf.	Average	Population	95% Conf.
Time	Time	(seconds)	•	Std. Dev.	Interval		Std. Dev.	Interval
0703:30	0712:13	524	4.59	1.54	0.13	3.68	2.99	0.26
0712 14	0712 42	29	59.33	13.87	5.05	23.85	2.72	0.99
0712:43	0712-54	12	24 30	3 89	2.20	30.48	1.03	0.58
0712:55	0718:46	352	77 75	33.26	3 47	43.17	10.90	1.14
0718:49	0719.02	14	37 94	4 41	231	19.42	0.63	0.33
0719:02	0734.32	630	7 41	2.47	0.18	5.41	3.74	0.24
0719.03	0734.32	300	81 59	20.00	410	33.62	5 79	0.79
0734.33	0737,59	207	14.00	3.04	0.48	14 02	4 80	0.60
0735:00	0742:12	203	14.25	3.51	0.40	40.22	8 44	0.00
0742:13	0747:27	315	02.04	31.52	3.40	40.33	2.14	0.30
0/4/:28	0749:03	96	20.00	4.40	0.90	19.30	2.14	0.40
0749:04	0749:41	38	37.34	2.90	0.92	14.00	0.65	0.20
0749:42	0750:52	71	14.42	4.17	0.97	17.40	2.71	0.03
0750:53	0757:18	386	80.80	31.69	3.16	39.92	9.3/	0.93
0757:19	0757:31	13	27.98	1.09	0.59	23.20	0.33	0.18
0757:32	0757:43	12	34.79	3.29	1.86	22.13	0.34	0.19
0757:44	0757:51	8	26.41	1.79	1.24	21.32	0.21	0.15
0757:52	0758:03	12	33.51	1.73	0.98	20.70	0.14	0.08
0758:06	0758:13	8	32.19	0.98	0.68	20.51	0.03	0.02
0758 14	0758:27	14	26.94	1.62	0.85	20.61	0.09	0.05
0758 28	0758-34	7	32.56	0.99	0.74	20.92	0.13	0.10
0758-35	0758 38	Å	29.10	0.55	0.54	21.24	0.09	0.09
0758 20	0759.47	à	30.34	0.20	0.13	21 51	0 18	0.12
0758:48	0750.47	34	22.03	3 93	1.32	24 19	1 65	0.56
0750.40	0703.21	567	71 07	32.12	2.65	38 37	10.98	0.91
0/59.22	0006.43	502	19.65	3.25	0.53	45.26	1 78	0.29
0808:44	0811:05	142	10.00	3.23	1.30	13.20	0.10	0.23
0811:06	0811:12		47.70	1.07	1.35	12.09	3.04	0.57
0811:13	0814-52	220	17.79	3.36	0.44	12.39	3.94	0.52
0814:53	0823.52	540	72.20	35.88	3.03	37.83	12.34	1.04
0823:53	0823:56	4	28.16	1.02	1.00	18.92	0.04	0.04
0823:58	0824:14	17	27.92	.1.43	0.68	18.49	0.13	0.06
0824:15	0824:21	7	31.04	0.36	0.27	18.48	0.05	0.04
0824:22	0825:05	44	25.76	3.06	0.90	21.58	2.25	0.67
0825:07	0825:33	27	25.54	3.38	1.28	29.73	1.95	0.74
0825:34	0829:31	238	86.08	32.73	4.16	41.58	6.11	0.78
0829:34	0829:59	26	36.10	2.71	1.04	26.40	1.10	0.42
0830.01	0830:43	43	32.15	1.40	0.42	21.88	1.30	0.39
0830-44	0830 47	4	29.09	0.44	0.43	19.91	0.10	0.10
0830-48	0830-53	6	30.88	0.34	0.27	19.54	0.16	0.13
0830-54	0830-58	5	29.63	0.17	0.15	18.89	0.17	0.15
03.0280	0831.00	Ă	30 49	0.23	0.23	18.48	0.08	0.08
0030.55	0831.02		28 47	0.72	0 47	17 89	0.24	0.16
0031:03	0031.11	3	31 15	0.58	0.46	17.23	014	011
0831:12	0831:1/	174	17 76	2.30	0.40	15.02	202	0.43
0831:18	0834:11	1/4	82.77	2.43	1.5/	44.40	0.54	0.45
0834:12	0840:55	404	00.27	30.00	3.52	17.04	3.00 A 52	0.54
0840:56	0845:03	248	15.93	3.55	0.44	17.94	4.34	0.00
0845:04	0854:11	548	//.49	54.33	2.67	40.18	12.5/	1.05
0854:14	0854:21	8	31.34	0.68	0.47	19.71	0.11	0.08
0854:22	0854:45	24	27.75	0.90	0.36	19.07	0.38	0.15
0854:46	0854:49	4	31.31	0.62	0.61	18.51	0.15	D.14
0854:50	0855:12	23	27.30	1.96	0.80	18.05	0.30	0.12
0855:13	0855:16	4	30.87	0.45	0.44	17.59	0.06	0.06
0855 19	0855:25	7	30.96	0.67	0.50	17.20	0.07	0.05
0855-20	0855-38	9	28.27	0.68	0.44	16.82	0.09	0.06
0855 20	0855-41	3	31.16	0.17	0.19	16.62	0.02	0.02
0855.42	0856-16	35	26.05	2.24	0.74	16.33	0,35	0.12
0856.17	0856-10	1 1	30 77	0.26	0,30	15 77	0.02	0.02
0000:17	0010.42	864	17.29	4.07	0.27	11 16	3.35	0.22
0050:20	0910:43	404	72 01	36.52	3.47	37 02	8 80	0.84
0910:44	0917:49	420	87.40	41 52	457	45 27	10 42	1 15
0917:51	0923:07	31/	22.40	3.02	4.37	NU.27	0.42	0.10
0923:09	0923 17	9	33.14	2.03	1.55	24.61	0.30	0.19

Table C-4. THC Analyzer Results from June 23, 1993, First Period of Spraying

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(Continued)

Table C-4 Continued

June 2	3, 1993	Elapsed	11	LET THC (pp	(m)	OL	TLET THC (	ppm)
Start	End	Time	Average	Population	95% Conf.	Average	Population	95% Conf.
Time	Time	(seconds)		Std. Dev.	Interval		Std. Dev.	<u>interval</u>
0923:18	0923:28	11	25.22	2.10	1.24	23.59	0.47	0.28
0923:29	0924:17	49	36.10	4.57	1.28	20.41	1.39	0.39
0924:18	0926:28	131	18.82	2.39	0.41	17.22	2.22	0.38
0935:06	0935:37	32	38.65	3.85	1.33	20.68	0.42	0.14
0935:38	0935:44	7.	28.84	0.64	0.47	20.06	0.40	0.30
0935:45	0936:24	40	32.28	1.58	0.49	18.84	0.78	0.24
0936:25	0936:31	7	28.60	0.64	0.47	17.24	0.15	0.11
0936:32	0936:40	9	30.89	0.26	0.17	16.68	0.17	0.11
0936:43	0936:54	12	32.75	1.61	0.91	15.88	0.21	0.12
0936:55	0939:15	141	19.72	3.75	0.62	17.00	4.06	0.67
0939:16	0946:26	431	86.39	33.59	3.17	42.91	10.91	1.03
0946:27	0948:35	129	20.91	2.56	0.44	21.87	4.48	0.77
0948:36	0955:17	402	109.87	39.12	3.82	54.97	11.16	1.09
0955:18	0957:16	119	20.40	3.33	0.60	11.19	11.17	2.01
Emissions	> 30 PPM	5536	78.04			39.99		
Emissions	< 30 PPM	3829	15.83			13.22		
Alt	Emissions	9365	52.60			29.05		

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59.1% of time spent spraying, 0712 - 0957 • Outlier, from a period at the beginning of spraying.

June 2	3, 1993	Elapsed	IN	ILET THC (pp	m)	01	TLET THC (	ppm)
Start	End	Time	Average	Population	95% Conf.	Average	Population	95% Conf.
Time	Time	(seconds)	_	Std. Dev.	Interval		Ştd. Dev.	Interval
1030:00	1031:02	63	9.01	2.28	0.56	13.99	5.22	1.29
1031:03	1036:24	322	86.88	41.41	4.52	41.03	9.25	1.01
1036:25	1039:32	163	18.05	3.49	0.54	20.30	5.65	0.87
1039:40	1048:57	550	91.13	51.17	4.28	53.05	17.47	1.46
1048:58	1049:47	50	19.82	4.73	1.31	35.54	3.43	0.95
1049:48	1057:36	469	99.86	42.90	3.88	59.33	14.72	1.33
1057:37	1057:46	10	27.82	1.25	0.77	28.30	0.41	0.25
1057:47	1057:49	3	30.79	0.08	0.09	27.41	0.12	0.14
1057:50	1101:19	210	19.10	3.69	0.50	21.71	4.45	0.60
1101:20	1105:48	269	106.69	45.78	5.47	55.71	10.03	1.20
1105:49	1111:22	334	19.01	4.13	0.44	19.77	7.18	0.77
1111:23	1112:27	65	66.77	29.17	7.09	26.64	3.61	0.88
1112:28	1112:50	23	27.99	1.00	0.41	<b>36</b> .80	1.80	0.74
1112:51	1120:08	438	110.37	46.20	4.33	63.02	15.33	1.44
1120:09	1124:37	269	18.13	2.42	0.29	18.36	4.75	0.57
1124:38	1137:17	760	80.14	42.52	3.02	46.78	17.98	1.28
1137:18	1137:30	13	26.49	1.56	0.85	19.95	0.33	0.18
1137:32	1144:44	433	16.83	3.88	0.37	13.26	4.99	0.47
1144:45	1154:36	592	96.86	46.51	3.75	56.61	19.45	1.57
1154:37	1154:57	21	25.04	3.07	1.31	21.90	0.61	0.26
1154:58	1155:03	6	31.96	0.78	0.62	20.60	0.18	0.14
1155.04	1157:51	168	18.74	3.22	0.49	19.06	4.95	0.75
1157:52	1203:07	316	110.56	43.34	4.78	60.62	13.21	1.46
1203:08	1203:12	5	28.79	0.70	0.61	37.11	0.34	0.30
Emissions	> 30 PPM	3790	94.93		1	53.55		
Emissions	< 30 PPM	1762	18.22			18.75		
All	Emissions	<b>5</b> 552	70.58			42.51		

Table C-5. THC Analyzer Results from June 23, 1993, Second Period of Spraying

68.3 % of time spent spraying, 1030 - 1203

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1	June 2	3 1993	Flapsed	10	ILET THE (DO	m)	01	TLET THC (	(mac
	Start	End	Time	Average	Population	95% Conf.	Average	Population	95% Conf.
	Time	Time	(seconds)		Std. Dev.	Interval		Std. Dev.	Interval
			10000						
•	1220:37	1242:06	1290	4,64	2.57	0.14	10.33	11.15	0.61
	1242:07	1243:15	69	73.26	30.12	7.11	24.78	2.13	0.50
	1243:18	1243:25	8	31.32	0.54	0.38	30.95	0.69	0.48
	1243.26	1243:57	32	25.77	1.91	0.66	36.83	2.94	1.02
	1243:58	1254:07	610	90.64	50.85	4.03	53.72	19.99	1.59
	1254:09	1254:28	20	32.95	1.41	0.62	22.44	0.57	0.25
	1254:29	1254:44	16	27.68	0.97	0.48	20.85	0.37	0.18
	1254:45	1254:53	9	30.95	0.53	0.35	19.79	0.21	0.14
	1254:54	1259:18	265	17.37	3.90	0.47	14.98	3.46	0.42
	1259:19	1306:18	374	100.41	36.24	3.67	52.86	13.53	1.37
	1306:19	1306:22	4	29.76	0.17	0.16	31.41	0.10	0.10
	1306:23	1306:58	36	36.29	3.84	1.25	28.31	1.54	0.50
	1306:59	1307:02	4	29.32	0.28	0.28	25.56	0.26	0.26
	1307:05	1307:16	12	29.19	0.45	0.26	24.07	0.45	0.25
	1307:17	1307:23	7	31.54	0.76	0.56	22.91	0.23	0.17
	1307:25	1307:41	17	35.27	3.16	1.50	21.99	0.25	0.12
	1307:42	1308:51	70	18.53	4.09	0.96	28.57	5.11	1.20
	1308:52	1313:40	289	86.49	38.12	4.39	46.99	9.29	1.07
	1313:41	1317:31	231	19.07	<b>3.6</b> 6	0.47	19.46	5.12	0.66
	1317:32	1322:08	277	104.34	32.59	3.84	52.88	9.51	1.12
	1322:09	1322:11	3	29.27	0.27	0.31	33.93	0.21	0.24
	1322:12	1322:19	8	32.19	1.24	0.86	32.62	0.58	0.40
	1322:20	1324:09	110	20.62	4.37	0.82	24.37	2.68	0.50
	1324:12	1324:33	22	23.39	2.58	1.08	25.15	0.65	0.27
	1324:34	1327:38	185	58 51	26.09	3.76	25.52	3.06	0.44
	1327:39	1332:29	291	19.56	4.87	0.56	13.72	3.49	0.40
	1332:30	1337:47	318	105.16	33.60	3.69	47.05	9.54	1.05
	1337:49	1340:05	137	55.69	10.28	1.72	39.03	5.40	0.90
	1340:07	1344.26	260	153.61	50.59	6.15	71.00	10.36	1.20
	1344:27	1344:38	12	26.30	1.68	0.95	44.06	1.09	0.62
	1344:39	1344:42	4	32.26	0.93	0.91	41.19	0.50	0.49
	1344:43	1344:45	3	28.97	0.48	0.55	39.91	0.32	0.37
	1344:46	1344 48	3	30.83	0.55	0.63	36.95	0.30	0.33
	1344:49	1352:12	444	15.65	3.64	0.34	14.32	7.23	0.07
	1352:13	1356.34	262	108.98	41.70	5.05	48.00	10.97	1.33
1	1356:35	1357:13	39	25.48	2.30	0.72	35.10	0.90	0.30
1	1357:16	1357:49	34	19.46	4.02	1.35	34.19	0.75	0.23
_	1357:50	1403:20	331	93.00	41.34	4.45	44.13	7.93	0.05
1	1403:21	1415:00	700	4.60	60.0	U.49	5.6U	1.30	0.54
	F-siesie	. 20 0014	2004	05 15			49.48		
	Emissions	> 30 PPM	3224	18.67			18 44		
	EMISSIONS	< JU PPM	1092	60.87			38.55		
		Emissions	4610	09.01		I	30.33		

Table C-6. THC Analyzer Results from June 23, 1993, Third Period of Spraying

66.9 % of time spent spraying, 1242 - 1415 • Outlier, from periods at the beginning and end of spraying.

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[	June 2	4, 1993	Elapsed	11	LET THC (PD	m)	01	TLET THC (	ppm)
	Start	End	Time	Average	Population	95% Conf.	Average	Population	95% Conf.
	Time	Time	(seconds)	, ,	Std. Dev.	Interval	_	Std. Dev.	Interval
									-
•	0712:00	0742:39	1802	5.45	2.17	0.10	3.77	4.06	0.19
1	0742:40	0743:18	39	62.84	18.42	5.78	26.19	3.43	1.08
	0743:19	0743:28	10	28.13	1.44	0.89	33.07	0.67	0.41
	0743:29	0748:50	322	90.27	27.84	3.04	50.85	9.79	1.07
- (	0748:51	0754:11	321	12.12	2.68	0.29	14.14	6.06	0.66
	0754:12	0754:48	37	64.97	19.12	6.16	28.61	3.35	1.08
	0754:49	0754:54	6	28.14	0.94	0.75	35.03	0.41	0.33
	0754:55	0801:28	394	90.81	32.88	3.25	51.54	12.45	1.23
	0801:29	0805:30	242	12.18	2.69	0.34	15.00	5.00	0.63
	0805:31	0809:34	244	91.16	34.86	4.37	43.53	8.49	1.07
	0809:35	0813:20	226	14.19	2.83	0.37	21.08	7.78	1.01
	0813:21	0818:54	334	91.73	39,89	4.28	56.84	24.08	2.58
	0818:55	0822:44	230	15.40	2.96	0.38	21.39	19.84	2.56
	0822:45	0828:25	341	94.96	43.20	4.58	77.74	9.20	0.98
	0828:26	0828:31	6	26.94	1.03	0.82	65.82	0.24	0.19
	082832	0829:32	61	37.52	4.20	1.05	62.43	1.65	0.41
	0829:33	0829:35	3	29.38	0.34	0.39	59.44	0.07	0.08
	0829:36	0829:48	13	31.92	0.91	0.49	59.17	0.33	0.18
	0829.49	0829:52	4	29.60	0.30	0.30	58.30	0.14	0.14
	0829:53	0830:05	13	34.26	2.23	1.21	57.62	0.26	0.14
	0830:06	0830:09	4	28.69	0.66	0.65	57.05	0.04	0.04
	0830:10	0830:19	10	33.36	1.47	0.91	56.70	0.19	0.11
	0830:20	0830:23	4	28.68	0.82	0.80	56.33	0.04	0.04
	0830:24	0830;44	21	33.62	1.96	0.84	<b>5</b> 5.61	0.37	0.16
	0830:45	0830:50	6	27.37	1.19	0.95	54.87	0.11	0.09
	0830:51	0830:54	4	30.49	0.24	0.24	55.19	0.50	0.49
	0830:55	0831:34	40	28.33	0.87	0.27	54.09	0.70	0.22
	0831:35	0831:37	3	31.20	0.60	0.68	53.07	0.04	0.05
	0831:38	0831:59	22	26.49	1.60	0.67	52.73	0.21	0.09
	0832:00	0832:11	12	33.25	1.98	1.12	52.51	0.42	0.24
	0832:12	0833:14	63	25.99	1.64	0.40	50.47	0.79	0.19
	0833:17	0833:20	4	29.19	0.40	0.39	49.04	0.05	0.05
	0833:21	0833:23	3	30.65	0.22	0.25	48.87	0.05	0.06
	0833:24	0837:49	266	12.93	2.87	0.35	46 80	3.09	0.37
	0837:50	0842:12	263	92.19	40.92	4.95	68.43	7.14	0.86
	0842:13	0847:00	288	16.64	3.29	0.38	36.82	7.09	0.82
	0847:01	0853:27	387	103.22	44.81	4.46	67.83	14.42	1.44
	0853:28	0857:14	227	17.86	1.74	0.23	32.35	5.16	0.67
	0857:15	0903:28	374	91.49	39.56	4.01	56.72	10.98	1,11
	0903:29	0905:42	134	16.25	2.94	0.50	30.49	5.19	0.88
	0905:43	0911:13	331	114.19	47.18	5.08	63.96	10.65	1.15
	0911:14	0911:32	19	27.87	1.63	0.73	41.40	0.89	0.40
	0911:33	0911:36	4	30.72	0.35	0.35	40.07	0.46	0.45
	0911:37	0911:48	12	28.24	0.76	0.43	40.33	0.40	0.23
	0911:49	0912:09	21	38.02	3.25	1.39	40.66	0.62	0.27
	0912:10	0912:35	26	21.99	3.79	1.46	41.54	0.80	0.31
	0912:36	0920:47	492	97.09	44.23	3.91	<b>59.30</b>	15.40	1.36
	0920:48	0924:39	232	14.99	2.77	0.36	8.11	8.35	1.07
	0924:40	0924:59	20	33.52	1.48	0.65	1.08	0.04	0.02
	0925:00	0925:03	4	29.51	0.21	0.21	1.01	0.02	0.02
	0925:04	0925:28	25	34.40	1.76	0.69	2.29	1.46	0.57
	0925:29	0932:07	399	13.21	2.25	0.22	13.38	7.04	0.69
	0932:08	0937:02	295	104.13	42.75	4.68	62.99	13.29	1.52
	0937:03	0940:39	217	17.31	3.12	0.41	26.11	5.72	0.76
	0940:40	0948:59	500	83.77	32.49	2.85	51.59	6.44	0.56
	0949:00	0953:15	256	16.74	3.71	0.45	25.03	7.12	0.87
	0953 16	1000-30	435	87.61	41.58	3.91	54.99	14.05	1.32

Table C-7. THC Analyzer Results from June 24, 1993, First Period of Spraying

(Continued)

# Table C-7 Continued

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	June 2	4, 1993	Elapsed	INLET THC (ppm)			OUTLET THC (ppm)		
	Start	End	Time	Average	Population	95% Conf.	Average	Population	95% Conf.
	Time	Time	(seconds)		Std. Dev.	Interval		SId. Dev.	Interval
•	1000:31 1000:44 1001:01	1000:43 1001:00 1031:02	13 17 1802	28.53 32.96 7.48	0.61 1.74 4.36	0.33 0.83 0.20	28.81 26.89 7.78	0.49 0.64 3.80	0.27 0.31 0.18
	Emissions Emissions All	> 30 PPM < 30 PPM Emissions	5015 3284 8299	91.24 15.67 61.33			57.58 25.33 44.82		

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60.4 % of time spent spraying, 0742 - 1001 \* Outlier, from periods at the beginning and end of spraying.

June 2	4, 1993	Elapsed	11	LET THC (pp	m)	······ OL	TLET THC (	ppm)
Start	End	Time	Average	Population	95% Conf.	Average	Population	95% Conf.
Time	Time	(seconds)		Std. Dev.	Interval		Std. Dev.	Interval
							0.05	0.01
1033:47	1034:34	48	8.98	2.74	0.77	0.95	0.05	0.01
1034:35	1039:46	312	104.28	46.95	5.21	55.19	13.52	0.35
1039:47	1039:50	4	29.21	0.48	0.4/	42.07	0.20	0.23
1039.51	1041:26	96	38.61	3.54	0.71	34.00	6.02	0.00
1041:27	1044:39	193	23.06	2.01	0.28	23.18	5.05	1 0.71
1044:41	1053:18	519	97.59	58.98	5.07	28.89	22.41	0.28
1053.19	1053:22	4	29.84	0.08	0.08	29.39	0.20	0.20
1053:23	1053:27	5	30.24	0.07	0.06	30.94	4.52	1.48
1053:28	1054:03	36	20.97	1.00	5.77	39.01	40.00	1.40
1054:04	1101:22	438	125.05	4.22	0.72	30.64	0.62	0.34
1101:23	1101:35	13	20.55	1.00	0.72	28 50	0.56	0.32
1101:30	1101.47	12	31.00	0.34	0.72	27.03	0.23	0.19
1101.51	1107:55	6	29.63	0.35	0.28	26 30	0.26	0.21
1101:56	1102:01	5	20.00	0.55	0.13	25.57	0.17	0.15
1102:02	1102.00	249	16.64	5.55	0.69	17 84	5.02	0.62
1102.07	1112.12	350	131 94	58.08	6 01	71 59	18.37	1.90
1110.13	1112.13	33 <del>3</del>	28 77	0.55	0.38	39.06	0.65	0,45
1112.10	1112.21		30.76	0.45	0 44	37 34	0.19	0,18
1112:22	1112.20	5	28.92	0.51	0.45	36.25	0.31	0.27
1112.20	1112.30	6	31.87	1 15	0.92	34.86	0.52	0.42
1112.31	1112.30	335	19.49	5 20	0.56	17.91	6 67	0.71
1112.37	1124-15	364	104.31	58.37	6.00	54 45	15.05	1.55
1124-16	1124.19	4	29.75	0.25	0.25	27.79	0.15	0.15
1124:20	1124:42	23	33,76	1.69	0.69	25.98	0.90	0.37
1124.43	1125-11	29	27.81	1.30	0.47	23,23	0.65	0.24
1125.12	1125:15	4	30.30	0.07	0.06	22.29	0.06	0.06
1125 17	1125.28	12	31.52	0.70	0.39	21.67	0.24	0.14
1125 32	1125:45	15	31.68	0.64	0.32	21.06	0.17	0.09
1125:46	1126:00	15	27.38	1.17	0.59	20.34	0.25	0.12
1126:01	1126.23	23	34.38	2.09	0.85	19.39	0.30	0.12
1126-24	1128.50	147	19.64	3.92	0.63	18.77	3.74	0.60
1128:51	1130.21	91	81,65	45.55	9.36	31.48	2.58	0.53
1130:23	1130 46	25	25.81	2.57	1.01	42.34	2.34	0.92
1130 47	1134:40	234	109.15	63.24	8.10	57.42	10.67	1.37
1134:41	1134:47	7	27.72	1.30	0.96	33.93	0.54	0.40
1134:49	1135:31	43	27.11	1.11	0.33	28.91	2.13	0.64
1135:33	1135:41	9	29.30	0.36	0.23	25.05	0.32	0.21
1135:42	1136:22	41	34.63	2.07	0.63	22.61	1.13	0.35
1136:24	1136:45	23	28.66	0.64	0.26	20.12	0.42	0.17
1136:46	1136:53	8	31.22	0.64	0.45	19.27	0.31	0.21
1136.54	1138.29	96	20.04	3.79	0.76	18.22	2.70	0.54
1138:30	1141:14	165	88.80	48.02	7.33	39.09	4.93	0.75
1141:15	1141:36	22	28.03	1.10	0.46	31.21	1.23	0.52
1141:40	1141:47	8	30.43	0.16	0.11	28.01	0.37	0.25
1141:48	1142:01	14	29.26	0.56	0.29	26.63	0.47	0.25
1142:02	1142:23	22	31.36	0.57	0.24	24.24	1.03	0.43
1142:24	1146:31	248	19.63	4.28	0.53	16.60	4.62	0.57
1146:32	1153:55	444	123.56	61.56	5.73	62.24	17.48	1.63
1153:56	1156:22	147	21.92	2.73	0.44	16.94	8.91	1.44
1156:23	1206:00	578	81.84	37.49	3.06	40.56	23.57	1.92
1206:01	1206:18	18	29.14	0.90	0.42	24.78	0.52	0.24
1206:19	1206:26	8	30.86	0.51	0.35	23.51	0.18	0.12
1206:27	1207:15	49	25.07	2.44	0.68	21.18	1.08	0.30
1207:16	1207:18	3	30.51	0.19	0.22	19.27	0.09	0.10
1207:19	1209:45	147	19.55	3.98	0.64	8.94	8.37	1.35
	1							
Emissions	> 30 PPM	3806	100.78			54.27	l i	
Emissions	< 30 PPM	1796	20.94			19.86		
All	Emissions	5602	75.18		1	43.23		

Table C-8. THC Analyzer Results from June 24, 1993, Second Period of Spraying

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67.9 % of time spent spraying, 1034 - 1207 • Outlier, from periods at the beginning and end of spraying.

	June 2	4, 1993	Elepsed	11	ILET THC (PD	m)	01	TLET THC (	ppm)
	Start	End	Time	Average	Population	95% Conf.	Average	Population	95% Conf.
	Time	Time	(seconds)		Std. Dev.	Interval		Std. Dev.	<u>Interval</u>
•	1230:15	1244:15	841	5.45	2.63	0.18	6.16	3.09	0.21
	1244:16	1247:46	211	116.98	55.88	7.54	56.16	12.45	1.68
	1247:47	1251:57	251	21.52	4.05	0.50	24.12	9.35	1.16
	1251:58	1252:01	4	30.95	0.48	0.47	21.41	0.38	0.37
	1252:02	1252:36	36	22.89	2.23	0.74	30.28	4.92	1.63
	1252:37	1257:40	304	132.39	60.19	6.77	68.41	14.37	1.62
	1257:41	1304:26	406	20.10	5.03	0.49	17.88	7.43	0.72
	1304:28	1305:25	59	36.62	3.40	0.87	15.53	0.87	0.22
	1305:26	1305:42	17	29.15	0.83	0.39	17.65	0.33	0.16
	1305:45	1305:52	8	29.36	0.29	0.20	18.73	0.19	0.13
	1305:53	1305:57	5	30.90	0.46	0.41	19.22	0.18	0.16
	1305:59	1306:10	13	26.14	1.47	0.80	19.79	0.22	0.12
	1306:11	1307:25	75	43.30	7.09	1.60	19.98	1.06	0.24
	1307:26	1333:06	1541	12.62	4.09	0.20	8.90	3.77	0.19
	1333:07	1338:05	299	129.40	52.80	5.98	64.94	12.75	1.45
	1338:06	1339:43	98	21.62	3.45	0.68	34.37	3.32	0.66
	1339:44	1344:17	274	109.07	51.49	6.10	55.14	6.78	0.80
	1344:18	1346:00	103	21.39	2.85	0.55	33.22	3.55	0.69
	1346:01	1350:58	298	114.81	49.64	5.64	60.55	10.73	1.22
	1350:59	1352:03	65	22.03	3.40	0.83	39.46	2.17	0.53
	1352:04	1353:56	113	122.79	38.92	7.18	51.17	3.17	0.58
	1353:57	1354:04	8	26.55	1.22	0.85	43.61	0.63	0.43
	1354:05	1354:11	7	41.97	5.32	3.94	41,30	0.62	0.46
•	1354:12	1400:00	349	4.03	5.99	0.63	9.85	12.43	1.30
				1		1			
	Emissions	> 30 PPM	1649	113.75			<b>56</b> .93		
	Emissions	< 30 PPM	2545	16.05			15.13		
	All	Emissions	4194	54.46			31.56		

Table C-9. THC Analyzer Results from June 24, 1993, Third Period of Spraying

39.3 % of time spent spraying, 1244 - 1354 • Outlier, from periods at the beginning and end of spraying.

## APPENDIX D

# RESULTS OF CHEMICAL ANALYSES OF WATER AND SCRUBBER LIQUID SAMPLES

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Table D-1. Analysis of Sample from Scrubber Chamber #1, 6/23/93 at 1340 hours

Date Samp	oled:	Jun 23, 1993	Sample	ID:	Scrubber Tank 1, Sa	mple #5, H438-27-7
Date Analy	zed:	Aug 25, 1993	SRI Run	No.:	P03050	
Sample Siz	ze:	0.01 ml	Related	Blank:	P02642	Surrogate
						(% Recovery)
				Amount	Concentration	or Det. Limt
Number	Com	pound		(NG)	(µG/L)	(μG/L)
17	1,2-0	lichloroethane-d4	SURR1	187	37.3	74.7
26	tolu	ene-d8 SURR2		258	51.5	103
40	4-br	omofluorobenzene	SURR3	256	51.3	103
1	chlor	omethane		U	U	1255
2	vinyl	chloride		U	U	885
3	brom	nomethane		U	U	3475
4	chlor	oethane		U	U	2510
5	1,1-0	lichloroethene		U	2170	
6	acete	one		U	U	3640
7	meth	iyl iodide		υ	U	1600
8	carb	on disulfide		U	U	1400
9	meth	ylene chloride		U	U	2610
10	trans	-1,2-dichloroethene		U	U	865
11	1,1-0	lichloroethane		U	U	2170
12	2-bu	lanone		U	U	7300
13	brom	ochloromethane IS1	1	250	50	
14	chlor	oform		233	23300	410
15	1,1,1	-trichloroethane		U	U	7200
16	carbo	on tetrachloride		· U	U	5300
18	benz	ene		U	U	795
19	1,2-0	lichloroethane		U	U	780
20	1,4-0	lifluorobenzene IS2		250	50	
21	trichi	oroethene		U	U	1425
22	1,2-d	lichloropropane		υ	U	790
23	brom	odichloromethane		U	U	1185
24	cis-1	,3-dichloropropene		U	U	1225
25	2-he:	xanone		U	U	1545
27	tolue	ne		U	U	1010
28	trans	-1,3-dichloropropene	3	U	U	1320
29	1,1,2	-trichloroethane		U	U	1660
30	tetra	chloroethene		U	U	1440
31	4-me	thyl-2-pentanone		U	U	2065
32	dibro	mochloromethane		U	Υ U	4425
33	chlor	obenzene-d5 IS3		250	50	
34	chlor	obenzene		U	U	1380
35	ethyl	benzene		U	U	1085
36	m- & p-xylene			U	U	1020
37	o-xylene			U	U	<b>9</b> 45
38	styrene			U	U	705
39	brom	oform		U	U	2545
41	1,1,2	,2-tetrachloroethane		U	U	3135

## Table D-2. Analysis of Sample from Scrubber Chamber #2, 6/23/93 at 1340 hours

Date Sampled:		Jun 23, 1993	Sample ID:		Scrubber Tank 2, Sample #6, H438-28-1		
Date Analyzed:		Aug 25, 1993	SRI Run	No.:	P03051		
Sample Size:		0.100 ml	Related	Blank:	P02034	Surrogate	
						(% Recovery)	
				Amount	Concentratio	on or Det. Limt	
Number	Com	Ipound		<u>(NG)</u>	(μG/L)	(μG/L)	
17	1,2-0	lichloroethane-d4 S	URR1	180	35.9	71.8	
26	tolu	ene-d8 SURR2		254	50.8	102	
40	4-br	omofluorobenzene S	SURR3	239	47.9	95.8	
1	chlor	romethane		υ	U	125.5	
2	vinyl	chloride		U	U	88.5	
3	brom	nomethane		υ	U	347.5	
4	chloi	roethane		U	U	251.0	
5	1,1-0	lichloroethene		U	U	217.0	
6	acete	one		70.9	709	364.0	
7	meth	yl iodide		υ	U	160.0	
8	carb	on disulfide		U	U	140.0	
9	meth	ylene chloride		U	U	261.0	
10	trans	-1,2-dichloroethene		U	U	86.5	
11	1,1-0	lichloroethane		U	U	217.0	
12	2-bu	tanone		U	U	730.0	
13	brom	nochloromethane IS1		250	50		
14	chior	roform		3940	39400	41.0	
15	1,1,1	-trichloroethane		U	U	720.0	
16	carb	on tetrachloride		· U	U	530.0	
18	benz	ene		U	U	79.5	
19	1,2-0	lichloroethane		υ	U	78.0	
20	1,4-0	lifluorobenzene IS2		250	50		
21	trichl	oroethene		U	U	142.5	
22	1,2-0	lichloropropane		U	U	79.0	
23	brom	odichloromethane		U	U	118.5	
24	cis-1	,3-dichloropropene		U	U	122.5	
25	2-he	xanone		U	U	154.5	
27	tolue	ne		U	U	101.0	
28	trans	-1,3-dichloropropene		U	U	132.0	
29	1,1,2	-trichloroethane		υ	U	166.0	
30	tetra	chloroethene		U	U	144.0	
31	4-me	thyl-2-pentanone		U	U	206.5	
32	dibro	mochloromethane		U	U	442.5	
33	chlor	obenzene-d5 IS3		250	50		
34	chlor	obenzene		U	U	138.0	
35	ethyl	benzene		U	U	108.5	
36	m- &	p-xylene		U	U	102.0	
37	o-xvl	ene		U	U	94.5	
38	styre	ne		U	U	70.5	
39	brom	oform		U	U	254.5	
41	1,1,2	2-tetrachloroethane		U	U	313.5	

Table D-3. Analysis of Sample from Scrubber Chamber #1, 6/24/93 at 1040 hours

Date Sampl	ed: Jun 24, 1993 Sample		ID: Scrubber Tank 1, San		nple #7, H438-28-2	
Sample Siz	e: 0.05 ml	Related	Blank:	P02642	Surrogate (% Recovery)	
			Amount	Concentration		
Number	Compound		(NG)	Light		
17	4.2 dichloroethene d		(110)	(µ3/L)	76	
26	toluono de SUPPo	+ SURRI	150	J0 824	104	
20	A bromofluorobonnor	A SUPP?	200	02.1 40 e	00.4	
40	4-biomothono	IE JURKS		43.0		
2	vinul chlorida		0	U U	477	
2	bromomethane		ŭ	Ŭ	605	
3	chiomethane		0	U U	502	
	1 1 dichloroathana		U U	0	JUZ 424	
S S	acetope		95.5	1010	728	
7	methyl indide		95.5 11	1310	320	
8	carbon disulfide		52	104	280	
Ğ	methylene chloride		J.Z.	11	522	
10	trans_1 2-dichloroethen	. a		0	173	
11	1 1-dichloroethane		Ü	U U	434	
12	2-butanone		2670	53400	1460	
13	bromochloromethane I	S1	250	50	1400	
14	chloroform		11 5	230	82	
15	1 1 1-trichloroethane		U	11	1440	
16	carbon tetrachloride		ŭ	Ŭ	1060	
18	benzene		ŭ	U U	159	
19	1 2-dichloroethane		Ŭ	Ŭ	156	
20	1 4-difluorobenzene IS	2	250	50		
21	trichloroethene	-		1	285	
22	1 2-dichloropropane		ŭ	ü	158	
23	bromodichloromethane	•	ŭ	ŭ	237	
24	cis-1 3-dichloropropene	2	ŭ	Ŭ	245	
25	2-hexanone		ŭ	Ŭ	3090	
27	toluene		ŭ	Ŭ	202	
28	trans-1.3-dichloroprope	ne	Ū	Ŭ	264	
29	1.1.2-trichloroethane		Ū	Ū	332	
30	tetrachloroethene		Ŭ	Ŭ	288	
31	4-methyl-2-pentanone		Ū	Ū	4130	
32	dibromochloromethane		Ū	Ŭ	885	
33	chlorobenzene-d5 IS3		250	50	• •	
34	chlorobenzene		U	Ū	276	
35	ethylbenzene		Ū	Ū	217	
36	m- & p-xylene		Ū	Ū	204	
37	o-xylene		U	Ŭ	189	
38	styrene		51.1	1022	141	
39	bromoform		U	U	509	
41	1,1,2,2-tetrachloroethai	ne	U	U	627	

## Table D-4. Analysis of Sample from Scrubber Chamber #2, 6/24/93 at 1040 hours

Date Sample	ed: Jun 24, 1993	Jun 24, 1993 Sample ID: Aug 26, 1993 SPI Pup No.		Scrubber Tank 2, Sample #8, H438-29-3		
Sample Size	: 5 ml	Related Blank:	P02034	Surrogate (% Recovery) or Det, Limt		
		Amouu	nt Concentration			
Number (	Compound	(NG	) (uG/L)	(uG/L)		
17	1 2-dichloroethane-d4 SI	IRR1 184	36.9	737		
26 1	oluene_d8 SURR2	257	51 3	103		
40	Lhromofluorohenzene S	URR3 242	48.4	96 7		
1	chloromethane			2 51		
2	vinvl chloride	U U	Ŭ	1 77		
3	bromomethane	U U	Ŭ	6.95		
4	chloroethane	Ű	ŭ	5 02		
5	1 1-dichloroethene		Ŭ	4 34		
6 1	acetone	12200	D 2440	7 28		
7 1	methyl iodide	U	U	3.2		
8 4	carbon disulfide	U U	Ŭ	2.8		
9 1	nethvlene chloride	Ŭ	ŭ	5.22		
10 1	rans-1.2-dichloroethene	Ū	Ū	1.73		
11	1.1-dichloroethane	Ū	Ŭ	4.34		
12 2	2-butanone	1830	367	14.6		
13	promochloromethane IS1	250	50			
14 (	chloroform	8.25	1.65	0.82		
15	1.1.1-trichloroethane	U	U	14.4		
16 0	carbon tetrachloride	. Ŭ	Ū	10.6		
18 1	penzene	U	U	1.59		
19 <sup>·</sup>	1,2-dichloroethane	U	Ŭ	1.56		
20	, 4-difluorobenzene IS2	250	50			
21 t	richloroethene	U	U	2.85		
22	1,2-dichloropropane	U	U	1.58		
23 I	promodichloromethane	U	U	2.37		
24 (	cis-1,3-dichioropropene	ບ	U	2.45		
25 2	2-hexanone	U	U	30.9		
27 t	oluene	U	U	2.02		
28 t	rans-1,3-dichloropropene	U	U	2.64		
29 <sup>-</sup>	1,1,2-trichloroethane	U	U	3.32		
30 t	etrachloroethene	U	U	2.88		
31 4	I-methyl-2-pentanone	U	U	41.3		
32 0	libromochloromethane	U	U	8.85		
33 (	chlorobenzene-d5 IS3	250	50			
34 0	chlorobenzene	U	U	2.76		
35 e	ethylbenzene	U	U	2.17		
36 r	n- & p-xylene	U	U	2.04		
37 (	≻xylene	U	U	1.89		
38 5	styrene	U	U	1.41		
39 t	promoform	U	U	5.09		
<b>41</b> 1	1,2,2-tetrachloroethane	U	U	6.27		

Date Sampled:		d: Jun 24, 1993 Sample		ID: Scrubber Tank 3, Sar		mple #9, H438-29-2	
Date Analy	zed: Aug 26, 1993		SRI Rur	n No.:	P03059		
Sample Si	ze:	5 ml	Related	Blank:	P02034	Surrogate	
						(% Recovery)	
				Amount	Concentration	or Det. Limt	
Number	Соп	ipound		(NG)	(µG/L)	(μG/L)	
17	1,2-(	dichloroethane-d4	SURR1	179	35.7	71.5	
26	tolu	ene-d8 SURR2		256	51.1	102	
40	4-br	omofluorobenzene	SURR3	240	48	95.9	
1	chlo	romethane		U	υ	2.51	
2	viny	l chloride		U	U	1.77	
3	bron	nomethane		U	U	6.95	
4	chlo	roethane		υ	U	5.02	
5	1,1-0	lichloroethene		U	U	4.34	
6	acet	one		37.1	7.41	7.28	
7	meth	nyl iodide		U	U	3.2	
8	carb	on disulfide		υ	U	2.8	
9	meth	nylene chloride		U	U	5.22	
10	trans	s-1,2-dichloroethene		U	U	1.73	
11	1,1-0	dichloroethane		U	U	4.34	
12	2-bu	tanone		U	U	14.6	
13	bron	nochloromethane IS:	1	250	<b>5</b> 0		
14	chlo	roform		36.5	7.31	0.82	
15	1,1,1	I-trichloroethane		U	U	14.4	
16	carb	on tetrachloride		U U	υ	10.6	
18	benz	ene		U	U	1.59	
19	1,2-0	lichloroethane		U	U	1.56	
20	1,4-0	difluorobenzene IS2		250	50		
21	trich	loroethene		U	U	2.85	
22	1,2-0	lichloropropane		U	U	1.58	
23	brom	nodichloromethane		U	υ	2.37	
24	cis-1	,3-dichloropropene		U	U	2.45	
25	2-he	xanone		U	U	30.9	
<b>2</b> 7	tolue	ine		U	U	2.02	
28	trans	-1,3-dichloropropen	e	U	U	2.64	
29	1,1,2	2-trichloroethane		U	U	3.32	
30	tetra	chloroethene		U	U	2.88	
31	<b>4-</b> me	ethyl-2-pentanone		U	U	41.3	
32	dibro	mochloromethane		U	U	8.85	
33	chior	robenzene-d5 IS3		250	50		
34	chlor	obenzene		U	U	2.76	
35	ethyl	benzene		U	U	2.17	
36	m- &	p-xylene		υ	U	2.04	
37	o-xy	ene		U	U	1.89	
38	styre	ne		U	U	1.41	
39	brom	noform		U	U	5.09	
41	1,1,2	2-tetrachloroethane	:	U	U	6.27	

# Table D-6. Analysis of Sample of Tap Water, 6/24/93 at 1015 hours

Date Samp Date Analy Sample Siz	oled: Jun 24, 1993 ized: Aug 25, 1993 ize: 5 ml	Sample ID: SRI Run No.: Related Blank:	Scrubber Process H <sub>2</sub> P03049 P02034	O, Sample #10, H438-27-6 Surrogate
		<b>A</b>	Constration	(% Recovery)
Number	Compound	Amouni (NG)		(uG/L)
17	1.2-dichloroethane-d4 SUE	R1 186	37.2	74.5
26	toluene-d8 SURR2	265	52.9	106
40	4-bromofluorobenzene SU	IRR3 277	55.4	111
1	chloromethane	U	U	2.51
2	vinvl chloride	Ŭ	Ŭ	1.77
3	bromomethane	Ū	Ū	6.95
4	chloroethane	U	Ŭ	5.02
5	1,1-dichloroethene	U	U	4.34
6	acetone	U	U	7.28
7	methyl iodide	U	U	3.2
8	carbon disulfide	U	U	2.8
9	methylene chloride	U	U	5.22
10	trans-1,2-dichloroethene	U	U	1.73
11	1,1-dichloroethane	U	U	4.34
12	2-butanone	U	υ	14.6
13	bromochloromethane IS1	250	50	
14	chloroform	<b>2</b> 75	55	0.82
15	1,1,1-trichloroethane	U	U	14.4
16	carbon tetrachloride	· U	U	10.6
18	benzene	U	U	1.59
19	1,2-dichloroethane	U	U	1.56
20	1,4-difluorobenzene IS2	250	50	
21	trichloroethene	U	U	2.85
22	1,2-dichloropropane	U	U	1.58
23	bromodichloromethane	60.8	12.2	2.37
24	cis-1,3-dichloropropene	U	U	2.45
25	2-hexanone	U	U	30.9
27	toluene	U	U	2.02
28	trans-1,3-dichloropropene	U	U	2.64
29	1,1,2-trichloroethane	U	U	3.32
30	tetrachloroethene	U	U	2.88
31	4-methyl-2-pentanone	U	U	41.3
32	dibromochloromethane	U	U	8.85
33	chlorobenzene-d5 IS3	250	50	
34	chlorobenzene	U	U	2.76
35	ethylbenzene	U	U	2.17
36	m- & p-xylene	U	U	2.04
37	o-xylene	U	U	1.89
38	styrene	U	U	1.41
39	bromoform	U	U	5.09
41	1,1,2,2-tetrachloroethane	U	U	6.27