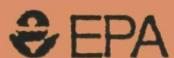


United States
Environmental Protection
Agency

Control Technology Center



EVALUATION OF THE POLYAD® FB
AIR PURIFICATION AND SOLVENT RECOVERY PROCESS
FOR STYRENE REMOVAL

control technology center



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AIR PURIFICATION AND SOLVENT RECOVERY PROCESS
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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, two processes have been developed to control styrene emissions and a short-term field evaluation was planned to characterize the styrene removal efficiency of pilot-scale versions of each process. Unfortunately, because only one system could be made available for the proposed test period, only one of these systems could be tested. 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 Polyad® fluidized bed (FB) air purification and solvent recovery system was quantified by continuously measuring the total hydrocarbon (THC) content of spray booth exhaust air entering and exiting the Polyad FB device with THC analyzers and by collecting NIOSH Method 1501/EPA Method 18 samples at the inlet and exit of the Polyad FB device. Styrene removal efficiencies greater than 90% were achieved.

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	in. H ₂ O
°C	1.8T + 32	°F
m	3.2808	ft
m ³	35.3134	ft ³
mmHg	0.03937	in. Hg
kg	2.2026	lb
1000 kg	0.90802	ton
m ³ /min	35.3134	ft ³ /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 technology had been demonstrated to control the emission of styrene.

The CTC was contacted by the firm of Weatherly, Inc., of Atlanta, GA, with regard to the possibility of evaluating a system (The Polyad® FB Process) that had been developed in Europe and is presently being used there to control styrene emissions. This process uses a fluidized bed adsorption system with proprietary macro porous polymer particles as the adsorbent. In the Polyad FB process the adsorbent continuously migrates from an adsorption section to a desorption section where the polymer particles are regenerated and the solvent is condensed and recovered back to the adsorption section.

After being contacted by Weatherly, Inc., 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 Environmental Technologies Corporation, of Northbrook, IL, to propose the evaluation of their chemical scrubber process (QUAD Chemtact™ System) along with the Polyad FB process on a source of styrene emissions. The QUAD Chemtact process removes 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 adsorbed into the mist of 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 the Polyad and Chemtact 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, Weatherly, and QUAD. 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 August visit, a tentative agreement was reached to test both the Polyad FB and Chemtact processes on a representative source of styrene emissions from the shower stall/bathtub construction process. Subsequently, during testing of the Polyad FB unit, it was found that QUAD Environmental could not supply the unit for testing within the time frame allotted for this work.

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 be used as a fire retardant. The final step of manufacture is to separate the finished fiberglass product from the mold.

The purpose of this project was to evaluate the performance of two pilot-scale devices designed to control styrene emissions. During this evaluation, each pilot-scale control device was to be 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. As indicated above, of the two devices selected for evaluation, only the Polyad FB device could be tested within the time allotted for this work.

To measure the styrene removal efficiency of the pilot-scale Polyad FB device, 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 ranging from one to two hours. 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 Polyad FB unit is shown along with the location of the van used for sampling and the generator used to provide power for the Polyad device.

Each stage of manufacture except for mold separation or "pulling" is carried out in a spray booth. At the Eljer facility the spray booths were not constructed in place but are prefabricated units manufactured by Binks, Inc. 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 actually several feet 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, to a large fan unit mounted outside 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 m³/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 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.

Gelcoat is a nominal mixture of 1/3 styrene monomer, 1/3 polyester resin, and 1/3 pigment. At the time of this test two colors of pigment were used: white and pink. About three minutes are required to coat a bath tub mold with gelcoat and five minutes are required to coat a shower stall mold with

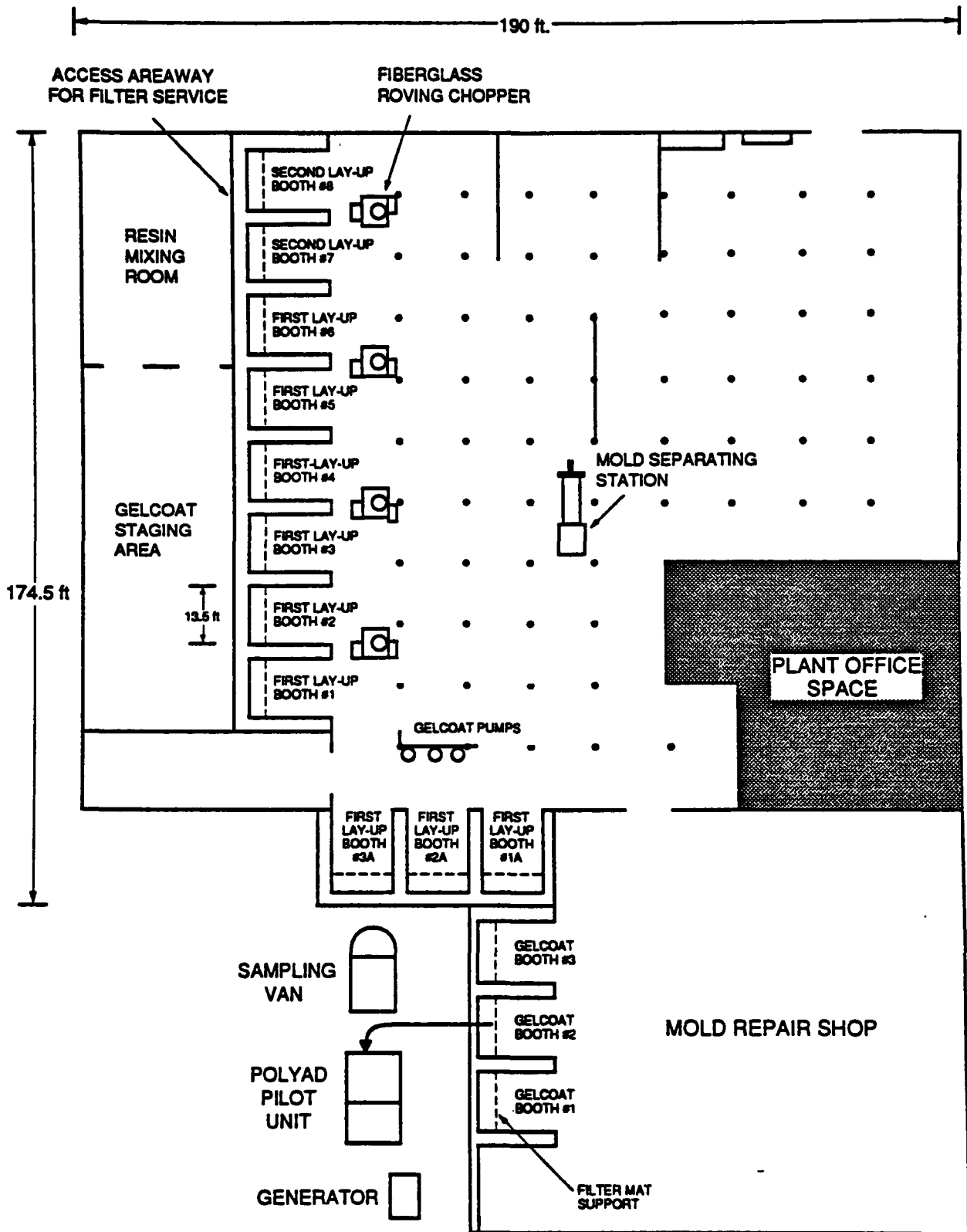


Figure 1. Layout of the Eljer Plumbingware Facility

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 its attached cart is 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. 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. In this step, calcium carbonate (CaCO_3) powder is added to a mixture of 50% styrene monomer and 50% polyester resin to form a slurry that contains approximately 50% solids. This slurry is sprayed onto the mold and during the spraying operation, chopped fiberglass roving is also blown at about a 30° angle into the stream of spray as it exits the spray nozzle. The spray mixes with the strands of chopped fiberglass and forms a entangled mat of resin impregnated fiberglass on the surface of the mold. The CaCO_3 powder and the chopped fiberglass help provide structural support to the finished product. 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 "backup" step and takes place in one of the two second lay-up booths shown in the upper left corner of Figure 1 (Booth #7 or Booth #8). In this step, a 60%-40% blend of powdered CaCO_3 and hydrated alumina is added to a mixture of 50% styrene monomer and 50% polyester resin to form a slurry that is contains approximately 50% solids. Hydrated alumina is added as a fire retardant. This mixture is also sprayed with chopped fiberglass fibers and forms the final layer on the mold. 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 set aside to cure for the final 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 to its final destination.

2.3 THE POLYAD® FB PROCESS

The Polyad FB process was developed and is marketed internationally by Nobel Chematur (now Chematur Engineering AB) of Karlskoga, Sweden. Weatherly, Inc., located in Atlanta, Georgia, is a wholly-owned subsidiary of Chematur International AB, and has the responsibility for domestic marketing and sales of the Polyad FB process. The pilot-scale Polyad FB device that was evaluated at the Eljer Plumbingware facility was provided and operated by Weatherly, Inc. who also supplied the information from which the following description of the Polyad FB process was taken.

Polyad is a collective name for adsorption processes developed by Chematur AB for the removal of organic substances from process exhaust air and water. These purification processes are all based on adsorption onto macro-porous polymer particles instead of activated carbon, which previously was the adsorption agent of choice for most solvent removal processes. Chematur indicates that Polymer adsorbents are superior to activated carbon because polymer formulations can be optimized for the adsorption of a specific solvent.

For air purification applications Chematur markets their proprietary macro-porous polymer under the trade name of Bonopore®. It is supplied in the form of off white to pale tan particles with an average size of 0.5 mm, bulk density of 0.3 g/cm³, and specific surface area of approximately 800 m²/g. The high surface area is due to the macro-porous nature of the material. The Material Safety Data Sheet for Bonopore indicates that it has a molecular weight > 1,000,000 and lists its components as divinylbenzene, ethylvinylbenzene, toluene, and water. Chematur indicates that the adsorption properties of Bonopore are unaffected by high humidity and that the polymer has no catalytic effect on solvents such as styrene. It also resists abrasion which is important as the Bonopore particles are generally used to constitute a bed that is fluidized with solvent-laden air. The amount of Bonopore required for a given application is governed by total air flow through the bed, the amount of solvent present in the air stream, the adsorption rate of the solvent onto the Bonopore polymer, and the desired solvent removal efficiency.

The Polyad FB (fluidized bed) air purification and solvent recovery process utilizes a continuously fluidized bed for air purification and the recovery of solvents from air. Chematur claims that

this process is especially well suited for recovery of solvents from air streams when the solvents have relatively high boiling points. Typical solvents that are suitable for removal with the Polyad FB process include aromatic and aliphatic hydrocarbons, chlorinated hydrocarbons, certain freons, alcohols, aldehydes, ketones, and esters. Organic solvents with low boiling points and very polar solvents, such as methanol or methylene chloride, are not suitable candidates for removal with the Polyad process.

At this time, two Polyad FB processes are marketed. The first of these processes is the one that was tested at Eljer Plumbingware where solvent is recovered for reuse or disposal. In this process (Figure 2) solvent-laden air is purified as it passes through a fluidized bed of Bonopore adsorbent. The saturated Bonopore adsorbent is then pneumatically conveyed to a desorption unit where it is regenerated.

The adsorption section consists of two, or more, beds of Bonopore. The number of beds depends on the type and concentration of the solvent and on the degree of solvent removal required. Solvent is adsorbed by the polymer particles as air passes through and fluidizes each bed. Bonopore continuously flows from one bed to the next. In the last bed the adsorbent, now saturated with solvent, is removed from the bottom of the bed and pneumatically conveyed to the desorption section at the same rate as regenerated Bonopore is fed into the first bed.

Bonopore from the adsorption section is pneumatically conveyed to the top of a vertical moving bed desorber or "stripper" for regeneration. The desorption section consists of a container mounted above the stripper unit comprising a specially designed heat exchanger with gas collector. As particles of Bonopore descend through the desorber they are heated in a heat exchanger to a temperature at which the solvent evolves. The heating medium is steam but, by using a heat exchanger, steam and water do not come in contact with the recovered sorbent or the Bonopore polymer. The vacuum created in the container at the top of the desorption section by the pneumatic transport fan causes air to be drawn in through an air intake at the bottom of the stripper. It is then drawn upward through the descending adsorbent. This air, together with the released solvent, is collected and directed into a condenser. Condensed solvent is captured in a tank. Air containing any uncondensed solvent is fed back into the top of the stripper and allowed to ascend again through the heated desorption zone.

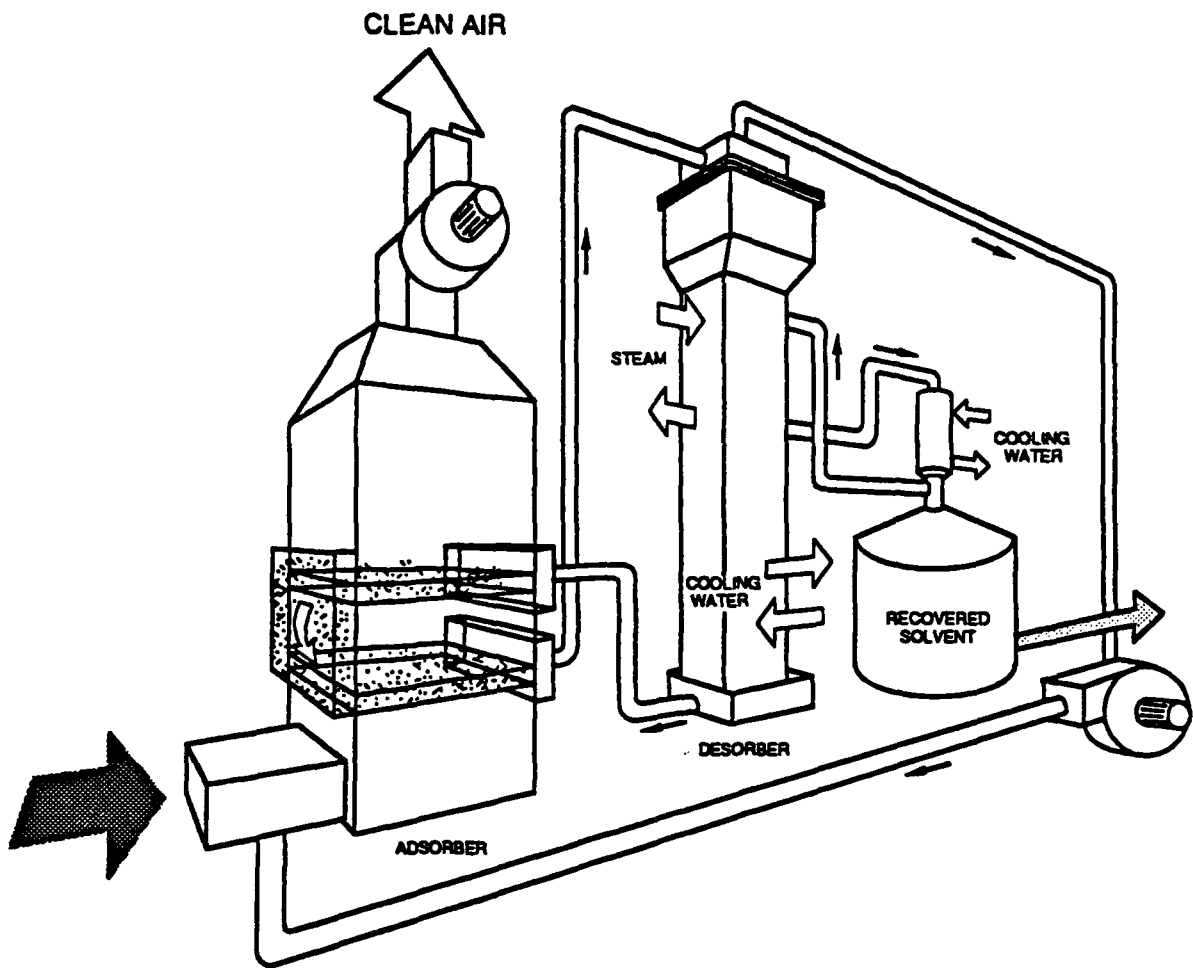


Figure 2. Diagrammatic representation of the Polyad FB Air Purification and Solvent Recovery Process.

Once past the heated section of the stripper, adsorbent is cooled by a water cooled heat exchanger situated at the bottom of the stripper. Ordinary tap water is usually sufficient to provide for satisfactory condensation of the recovered solvent. Regenerated adsorbent is pneumatically conveyed from the bottom of the desorber to the top of the adsorber into the first fluidized bed, to complete the cycle.

In a properly designed unit, essentially all of the solvent entering the unit will be adsorbed onto the Bonopore polymer before the process air stream carrying the solvent exits the Polyad FB unit. Therefore, outlet emissions are primarily due to sorbent "bleeding" from Bonopore polymer as it reenters the adsorber after being discharged from the desorber. This is because desorbed Bonopore is introduced back into the adsorption section at the last fluidized bed before the system outlet. Weatherly engineers emphasize that such outlet emissions can be minimized by proper design and are acceptable in light of the gain in design simplicity and reliability afforded by the use of gravity to aid in the feeding of Bonopore polymer from one fluidized bed to the next.

The second type of Polyad FB process is used in cases where solvent recovery is not required. In this case, the Polyad FB process is used as a preconcentrator to increase solvent concentration in the exhaust stream so that it can be easily incinerated. The net effect of such preconcentration is to reduce the total volume of air in the exit stream while increasing the concentration of solvent. For this application, the fluidized bed adsorber is unchanged but instead of a moving bed desorber a fluidized bed desorber is used. In the fluidized bed desorber the Bonopore is regenerated by blowing hot air through the adsorbent (in a fluidized bed) which causes the solvent to evolve. As with the first process, regenerated adsorbent is pneumatically conveyed back to the first adsorber. The hot solvent/air mixture leaving the desorber is passed to an incinerator where it is burned. To reduce energy consumption, a heat exchanger can be installed to recover waste heat at the incinerator outlet.

Among the Polyad FB units that have been installed, two were installed specifically to remove and recover styrene. One of these units was installed at the IFÖ-Sanitär AB plant in Bromölla, Sweden in 1989. This unit treats 21,200 m³/hr of air and can recover up to 8 kg/hr of styrene with a 90% overall

efficiency. This unit requires 52 kW of electric power, 0.5m³/h of cooling water and 150 kg of Bonopore catalyst per year. Another styrene removal/recovery unit was recently ordered (in Germany).

2.3.1 Pilot-Scale Polyad FB Device

The Polyad mobile unit used at the Eljer Plumbingware facility was designed to accommodate an air flow of up to 500 m³/h (294 acfm). With this unit configured as it was for this evaluation, a maximum steady state concentration of 1000 ppm of styrene could be accommodated before the level of outlet emissions would be affected. Short-duration peak concentrations of up to 3000 ppm of styrene could also be experienced before outlet emissions would be expected to increase. Solvent removal efficiency was expected to be greater than 90%. A schematic diagram of the pilot unit is shown in Figure 3 and a component arrangement drawing of the pilot unit is shown in Figure 4.

This portable unit consists of three separate modules designed to be assembled on site after being shipped there by truck. The total weight of the assembled package is 2000 kg and once set up it occupies a space 3.8 m long by 2.0 m wide by 5.0 m high. During operation the pilot-scale Polyad FB unit requires 45 kW of 480 VAC of electrical service, primarily for steam generation, fan power, and cooling water refrigeration. A separate generator is usually used to provide this service. The design cooling water pressure is 5 bar with a design volume flow of 200 l/h.

The pilot-scale unit uses four fluidized beds (two sections of two fluidized beds). Air that enters the unit passes first through a filter to remove foreign objects and then into the first fluidized bed. The filter housing also holds a heat exchanger to cool water used to condense recovered solvent. As shown in Figure 3, flow is upward. Clean air passes out of the top of the adsorber unit through a cyclone to the atmosphere. The cyclone catches any Bonopore adsorbent that escapes and feeds it back to the third fluidized bed.

Bonopore that has passed through the four fluidized beds is pneumatically conveyed to the top of the moving bed desorber unit. Excess air from the conveying process is routed back to the first fluidized bed at the inlet of the adsorber unit along with fluidizing air that is injected at the bottom of the desorber. The desorber incorporates two heat exchangers that are designed so that evolved solvents and the Bonopore adsorbent do not come into contact with the source of heating or cooling. The first

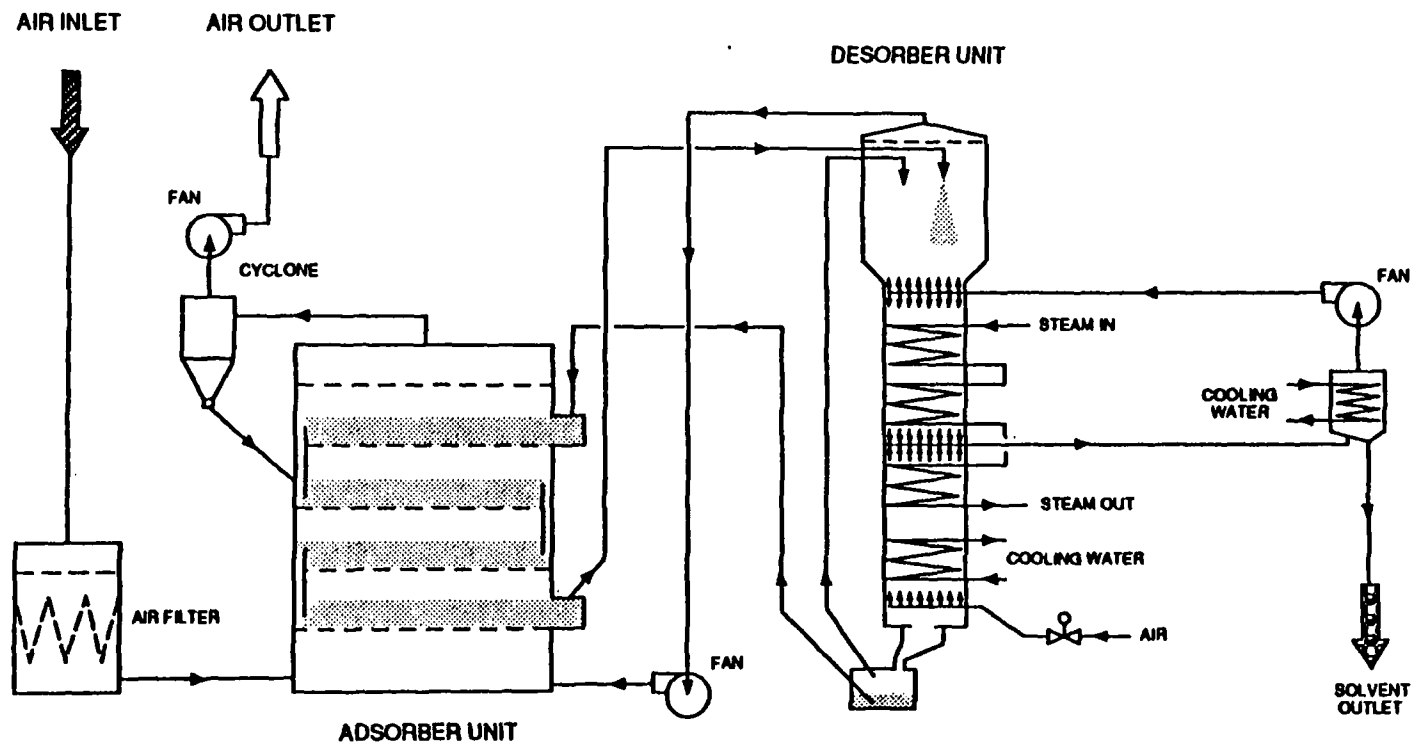
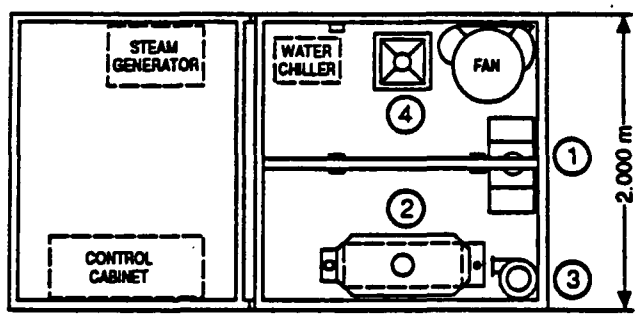
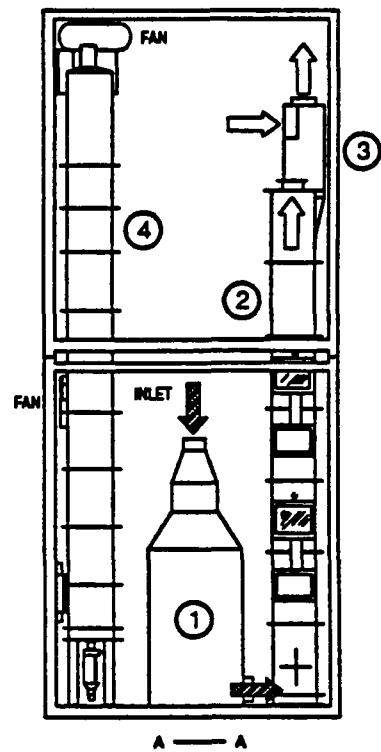
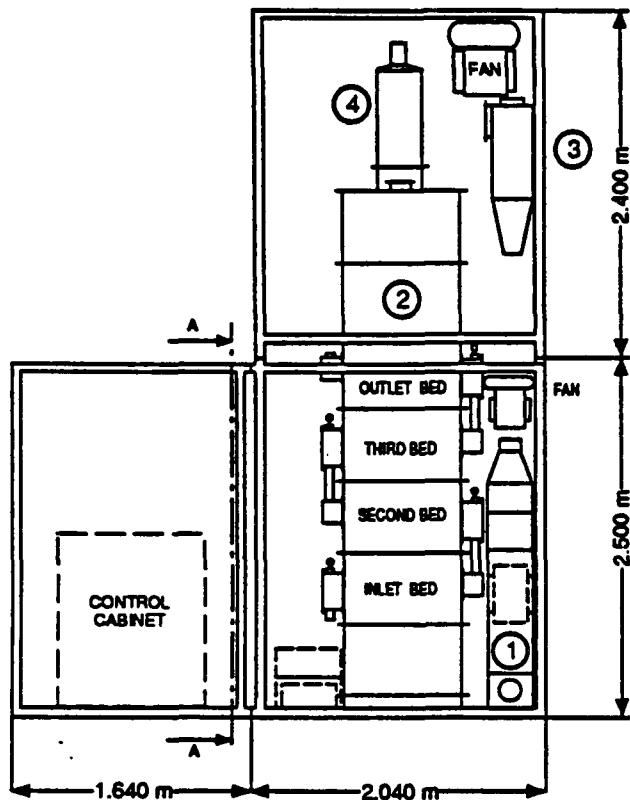


Figure 3. Schematic diagram of the pilot-scale Polyad FB unit tested at Eljer Plumbingware



PRINCIPAL COMPONENTS OF THE MOBILE POLYAD UNIT:

1. INLET PLENUM. INCORPORATES FILTER AND HEAT EXCHANGER FOR SOLVENT RECOVERY.
2. FLUIDIZED BED ADSORBER. INLET AT BOTTOM.
3. CYCLONE. RECOVERS BONOPORE ADSORBENT THAT ESCAPES FROM THE LAST FLUIDIZED BED. AIR DISCHARGED FROM CYCLONE TO ATMOSPHERE. CYCLONE CATCH ROUTED BACK TO THIRD FLUIDIZED BED.
4. DESORBER. BONOPORE ADSORBENT FROM OUTLET FLUIDIZED BED IS PNEUMATICALLY CONVEYED TO THE TOP OF THE DESORBER WHERE IT IS HEATED TO DESORB SOLVENT. REGENERATED ADSORBENT IS PNEUMATICALLY CONVEYED TO THE OUTLET FLUIDIZED BED.

Figure 4. Component layout of the pilot-scale Polyad FB unit tested at Eljer Plumbingware

(three-section) heat exchanger uses 135°C steam to evolve adsorbed solvent from the Bonopore polymer. The second (single-section) heat exchanger uses tap water to cool the Bonopore adsorbent back to room temperature (nominally 20 - 25°C) before it passes to the bottom of the desorber and is pneumatically conveyed back to the last section of the fluidized bed adsorber. The average time required for the Bonopore adsorbent to make one complete circuit of the system is one hour.

In the desorber, air and solvent evolved from the heated bonopore polymer is drawn from between the second and third section of the first heat exchanger and is sent to a separate water-cooled solvent condensing unit. Air that has passed through the condensing unit is returned to the inlet of the desorber to mix with incoming Bonopore adsorbent. Although tap water was used for this test, if it is required, an on-board refrigeration unit can supply chilled water (at 10°C) to the heat exchanger in the solvent condensing unit.

2.3.2 Specific Test Conditions

For this test the inlet air flow rate varied from 4.5 to 6.1 m³/min (159 to 215 acfm) at a pressure drop of from -2 to -2.5 kPa (-8 to -10 in. H₂O). The flow rate of Bonopore through the fluidized beds was kept at 10 kg/h (5.6 l/m, the lowest flow rate that can be maintained through the unit), except for one day (November 4) when the flow was set at 17 kg/h (9.4 l/m). The temperature of the desorber was set at 135°C (275°F), which is near, but below, the boiling point for styrene monomer (146°C). The tap water used for cooling the Bonopore adsorber and the heat exchanger in the solvent condensing unit averaged 20°C throughout the test. Table 1 summarizes the test conditions for each day of testing.

During analysis of VOC samples collected at the inlet and outlet of the pilot unit it was determined that while only styrene was present at the inlet of the Polyad FB device, substantial amounts of compounds other than styrene (mainly naphthalene and naphthalene derivatives) were present at the outlet. Through conversations with Weatherly, Inc. it was learned that this pilot unit had recently been tested at a naphtha manufacturing plant and that the Bonopore adsorbent used for that test was also used at Eljer. At the end of that test no special attempt was made to clean the unit or to desorb naphtha from the Bonopore adsorbent. At the beginning of this test VOC emissions at the outlet of the Polyad FB device were approximately 22% styrene. By the end of the test VOC emissions at the outlet of the

Table 1. Daily Test Conditions*

Date	Inlet Air Temp. (°C)	Rel. Humidity (%)	Inlet Air Flow (m³/min)	Bonopore Flow (kg/h)	Desorber Temp. (°C)
3 November	20-25	N/A	4.47	10	135
4 November	20-25	62 - 66	4.81	17	135
5 November	20-25	N/A	5.63	10	135

* System pressure drop of from -2 to -2.5 kPa (-8 to -10 in. H₂O)

Polyad FB device were approximately 85% styrene. A sample of recovered solvent obtained from the solvent condensing unit at the end of the test was approximately 26% styrene.

2.4 EXPERIMENTAL APPARATUS

2.4.1 Connection to the Pilot-Scale Polyad FB Unit

As is shown in Figure 1, the pilot-scale Polyad FB unit was installed on the outside of the plant as near as possible to the exhaust from gelcoat booth #2. Also shown in this drawing are the relative locations of a generator used to provide electrical power for the pilot unit and a small van used to house the sampling equipment used for this test. Figure 5 shows the overall arrangement for sampling. Approximately 19.5 m (64 ft) of flexible 15.24 cm (6 in.) diameter aluminum ducting was used to connect the Polyad FB unit on the ground to the exhaust of gelcoat booth #2 on the roof of the plant (approximately 4.6 m above the ground). Because outside temperatures were moderate (20 - 25°C) the ducting was not heated or insulated. A 0.9 m (3 ft) section of the same flexible aluminum ducting was attached to the outlet of the Polyad FB unit. All connections for the sampling equipment were made at the actual inlet and outlet of the pilot unit through rigid duct adapters and bulkhead fittings acquired for this test.

At the pilot unit inlet and outlet single 9.53mm (0.375 in.) diameter Teflon® sample lines were used to carry gas samples to the sample van for analysis. Both were about 2.13 m (7 ft) long. An unpublished EPA-sponsored styrene sampling effort determined that Method 18 sample lines did not need to be maintained near the boiling point of styrene but did need to be held at least 20°F above the local ambient temperature. Thus, the sample lines were maintained at a temperature of 49°C (120°F).

2.4.2 Sampling Van

Figures 6 and 7 show how the gas sampling equipment was connected within the van used to house the sampling equipment. Separate equivalent systems were constructed so that concurrent samples could be obtained at the inlet and the outlet of the Polyad FB device. Thus, the description that follows applies to either system.

Shortly after each 9.53mm diameter sample line entered the sampling van it was divided into two short 6.35 mm (0.25 in.) diameter sample lines less than 1 m in length. The smaller sampling lines

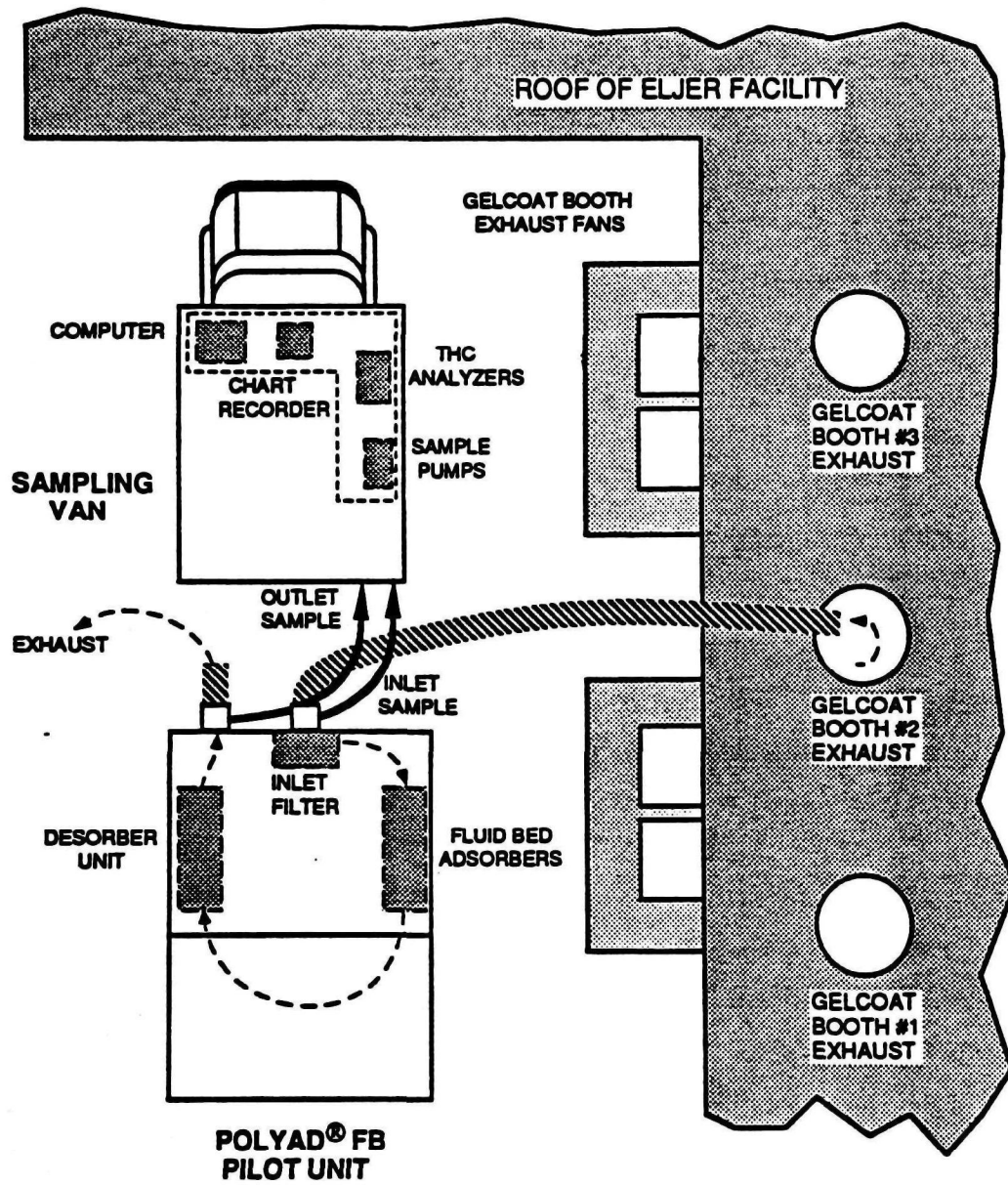


Figure 5. Overall arrangement for sampling at the Eljer Plumbingware Facility

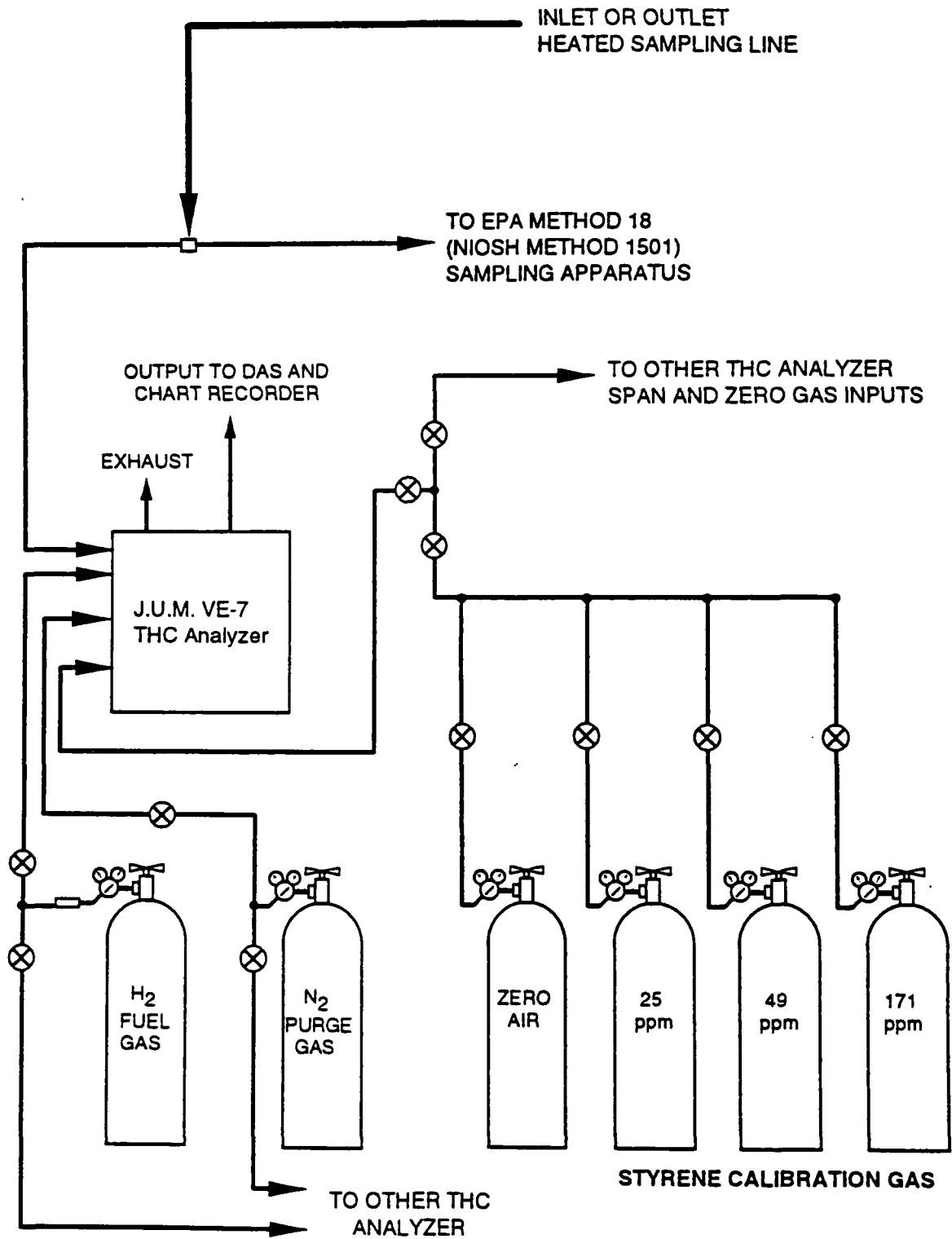


Figure 6. Equipment arrangement used for sampling with THC analyzers

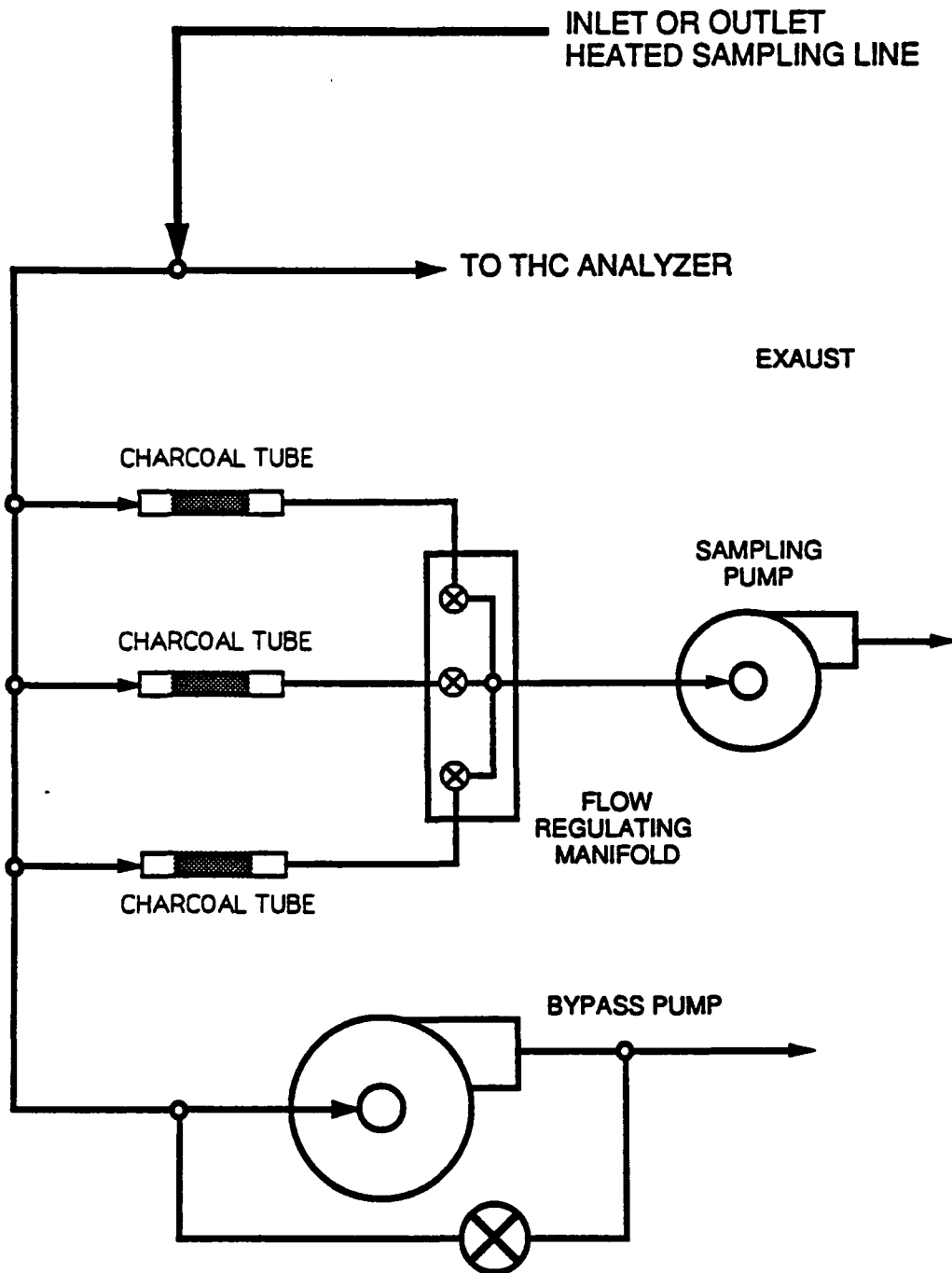


Figure 7. Equipment arrangement used for EPA Method 18 / NIOSH Method 1501 sampling

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 three Swagelock™ "Tee" connectors in series from which samples of gas could be withdrawn into charcoal-filled adsorption tubes (EPA Method 18, Section 7.4 or NIOSH Method 1501). After the last Tee connector this sample line was connected to a small 28.3 l/m (1 cfm) capacity sampling pump that was operated at approximately one-third of its rated flow. This pump served two purposes. The first purpose was to assure that more sample was withdrawn from the flexible aluminum duct than was required by the THC analyzer and the adsorption tube sample pump. The second purpose was to minimize the time required to convey a gas sample to the sampling equipment. The exhaust from this pump was diverted to the outside of the sample van.

Figure 6 shows the calibration gas system used for the THC analyzers. Three mixtures of styrene in nitrogen were used for calibration (171 ppm, 49 ppm, and 25 ppm), in addition to zero air. 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.

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 720 kb 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 (Labtech Notebook) 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 from 0 to 1000 ppm full scale and output from the outlet THC analyzer was displayed on a 0 to 100 ppm scale.

Preliminary measurements with charcoal-filled adsorption tubes (using NIOSH Method 1501, equivalent to the Adsorption Tube Procedure in Section 7.4 of EPA Method 18) made on a pre-test survey trip to Eljer Plumbingware revealed that virtually all (99%) of the organic material exhausted from the gelcoat spray booths was styrene monomer. During this test similar measurements were also made at the inlet and outlet of the Polyad FB device to quantify what organic compounds were present at the inlet and exhaust of this device. The primary intent of these measurements was to establish time-

averaged levels of styrene at the inlet and outlet of the Polyad FB device to determine the styrene removal efficiency of the Polyad FB device. As with the pre-test visit, NIOSH Method 1501 was followed in obtaining these samples (see Appendix A).

Figure 7 shows the equipment arrangement used for the NIOSH Method 1501 sampling. The same arrangement was used to obtain inlet and outlet samples. Provision was made to obtain three replicate samples at one time by taking a sample at each tee in the sample line that led to the bypass pump. The three samples were obtained with a single sampling pump connected to a manifold that, in turn, was connected to each tee through a standard small charcoal-filled tube. Flow through each leg of the manifold was set before each measurement to approximately 0.2 l/m.

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 the Polyad FB device (air exhaust from gelcoat booth #2) and exited the Polyad FB device. This analyzer extracts approximately 3 l/m of sample with an internal sample pump and sends from 17 to 20 cm³/m of that sample to an onboard FID. The FID's in these instruments were set up to use hydrogen as a fuel. Two of these THC analyzers were rented from Clean Air Engineering of Palatine, IL for the duration of testing. These instruments were inspected and calibrated with propane span gases before shipment.

Five decade output ranges can be 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 Polyad FB device was set to measure in the 0-1000 ppm range and the instrument used to monitor air exhausted from the Polyad FB 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, 49 ppm, and 25 ppm, certified by

Matheson® Gas Products, Inc) 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 were made at the back panel of the instrument and calibration and zero gas pressures were maintained at 1 bar (15 psig). Fuel gas (hydrogen) pressure was maintained at 1.5 bar (21 psig). 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 Volatile Organic Compound 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 volatile organic compounds (VOCs) from air that entered the Polyad FB device (air exhaust from gelcoat booth #2) and exited the Polyad FB device. NIOSH Method 1501 was followed for the analysis of the samples. A copy of the NIOSH procedure is included in Appendix A.

As shown in Figure 7, 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 bypass pump through three tee fittings where VOC samples were taken. Flow through the bypass pump was set (by restricting an internal bypass loop between the inlet and outlet of the pump) at a level only high enough to provide a small excess flow when the THC analyzer and adsorption tube samples were taken. Typically, the THC analyzer required 3 l/m and the three adsorption tube samples required a total of 0.6 l/m.

Three samples were taken at a time (to provide replicate samples, one sample from each tee) and concurrent measurements were made at the inlet and outlet of the Polyad FB device. The three samples were obtained with a single sample pump connected to a flow-regulating manifold. This manifold is designed so that up to three samples can be obtained with a single sample pump (SKC Model 224-26-03 adjustable low flow controller). Provision is made for internal regulation of each sample flow. At each tee, a standard small charcoal tube (SKC Model 226-01 charcoal-filled tube,

NIOSH approved, Lot 120) was connected to one side of the tee with the other side connected to the flow regulating manifold.

Before sampling commenced flow through each leg of the manifold was set to approximately 0.2 l/m. This was done by inserting a "dummy" small charcoal tube into the flow path after a bubble flow meter (Gilian Instruments Primary Flow Calibrator, 20 cm³/min to 6 l/m). A dummy tube could be used because the flow resistance properties of the NIOSH-approved charcoal-filled sample tubes are designed to be uniform from tube to tube. After calibration was completed, the dummy tubes were replaced with previously numbered charcoal-filled tubes. To prevent contamination, these sample tubes 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 one to one and one-half hours. 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, they were kept at room temperature until their contents were extracted for analysis.

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 NIOSH Method 1501, reproduced in Appendix A) followed by injection into a gas chromatograph (GC) coupled to an FID. In addition, several styrene standards were used to spike randomly selected charcoal-filled tubes and these samples were analyzed according to the NIOSH method to determine a desorption efficiency specific to this lot of charcoal-filled tubes (91.23%). 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.

2.5.3 Collection of Recovered Solvent Sample

A sample of liquid desorbed from the Bonopore adsorbent (2.6 liters) was collected at the end of the test from the reservoir in the Polyad FB device. The liquid had the approximate color of new motor

oil but a viscosity more like that of light cooking oil. The liquid had a pronounced unpleasant odor, not necessarily that of styrene monomer.

The liquid was brought back to SRI's Birmingham, Alabama laboratories for analysis. A sample of the liquid was diluted with carbon disulfide and subjected to GC-FID analysis to determine styrene content. A second sample of the liquid was subjected to GC analysis with mass spectrographic detection to determine what other compounds were present.

2.5.4 Total Flow Rate Measurements

During each day of testing, the total flow rate into the Polyad FB unit was measured with a thermal anemometer that had been calibrated in a wind tunnel at SRI's laboratories in Birmingham, Alabama before being taken into the field. These measurements were made at the inlet of the Polyad FB device 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 cm² (0.180 ft²). To measure flow, air velocity measurements were made at five evenly spaced points across the small duct, the measurements were repeated (except on the first day of testing), and the readings were averaged. The averaged air velocity measurement was then converted to volumetric flow. The daily average results of these measurements are shown in Table 1. 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. On the last day of testing a 15 minute power failure at 1:18 pm resulted in the loss of all data to the datalogger for the balance of the day. Data were reconstructed from the chart recorder record (which itself was lost while the power was off) by scanning the inlet and outlet record into computer files that were analyzed by specialized software to determine the numerical value of the data recorded during that time. The recovered data were then imported into the software package used to generate the experimental record presented in this report.

Some operational problems were encountered with the THC monitors. On the morning of the first day of sampling, November 3, 1992, the THC used to monitor hydrocarbon emissions at the inlet of the Polyad FB device experienced an abrupt shift in output (by a factor of 1.75). The exact reason for this behavior was not known but from an examination of the chart recorder record it was clear that the shift occurred shortly after the first calibration of the morning. It was detected (and corrected) at the lunchtime calibration. A correction factor was determined and the morning's data were corrected during analysis of the data. The THC at the outlet of the Polyad FB unit did not exhibit this behavior. The fact that both of these analyzers were calibrated at the same time with the same calibration gas allowed the problem to be quickly isolated and corrected. The same behavior (in the inlet THC analyzer) was observed one other time, during the calibration check at the end of the day on November 3. The problem did not appear again and in this instance did not affect any results. Afterwards, the behavior of this monitor was closely monitored.

The THC analyzer used to monitor hydrocarbon emissions at the outlet of the Polyad FB device experienced problems with FID flame-outs. The problem worsened until on November 5, technicians at Clean Air Engineering, Inc. provided guidance on how to correct the problem and the problem was fixed.

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 Polyad FB device instantaneous hydrocarbon emissions (essentially 100% styrene) ranged from as low as 90 ppm to as high as 400 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 18 ppm to 45 ppm. During midday lunch breaks in the production process, hydrocarbon levels decreased to approximately 9 ppm.

Figures 8 through 10 show output from the inlet THC analyzer that was recorded on the datalogger for the three days of testing, November 3 through 5, 1992. For clarity, THC data taken during periods of calibration are not shown.

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 (starting at about 0845) 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 1145. The final period starts around 1230 and lasts until 1415.

In order to show the variability and the periodic nature of the emissions from this process, inlet THC data from two 40 minute periods before the lunch break on November 5 are presented in Figures 11 and 12. Because these data have a one-second resolution in time, emissions from the spraying process can be resolved in some detail. With the exception of the second period of spraying shown in Figure 11, the operator spent from four to five minutes spraying gel coat on the mold. In the case of the second spraying period in Figure 11 and the periods of spraying shown in Figure 12 the operator spent from five to six minutes spraying gel coat on the mold and the pattern of emissions appears distinctly different between the two types of spraying. Whether these differences are due to differences in the type of mold (bath tub versus shower stall) or to the approach used by the operator cannot be determined because no attempt was made to track what type of mold was being sprayed.

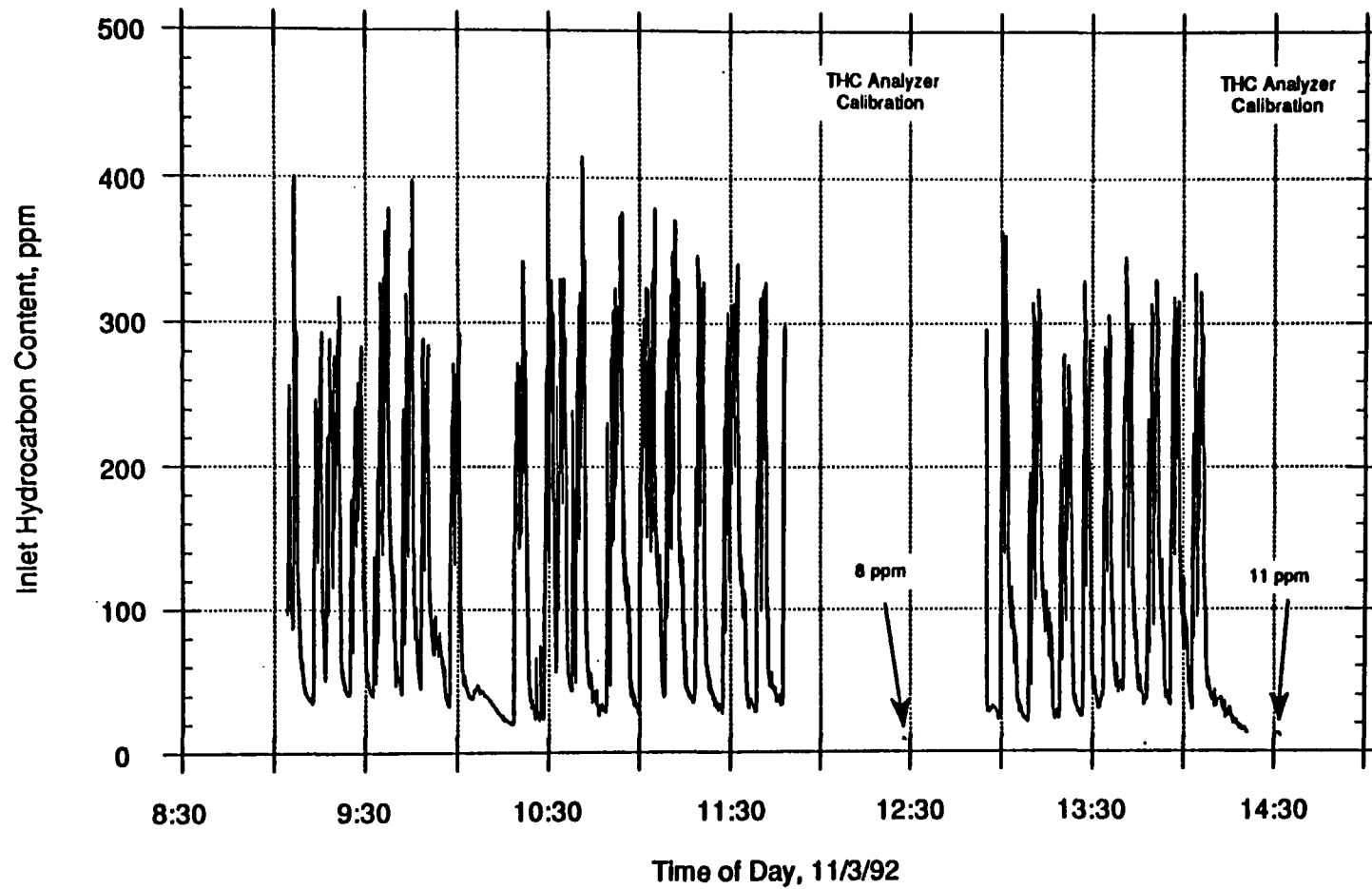


Figure 8. Inlet hydrocarbon emissions, November 3, 1992

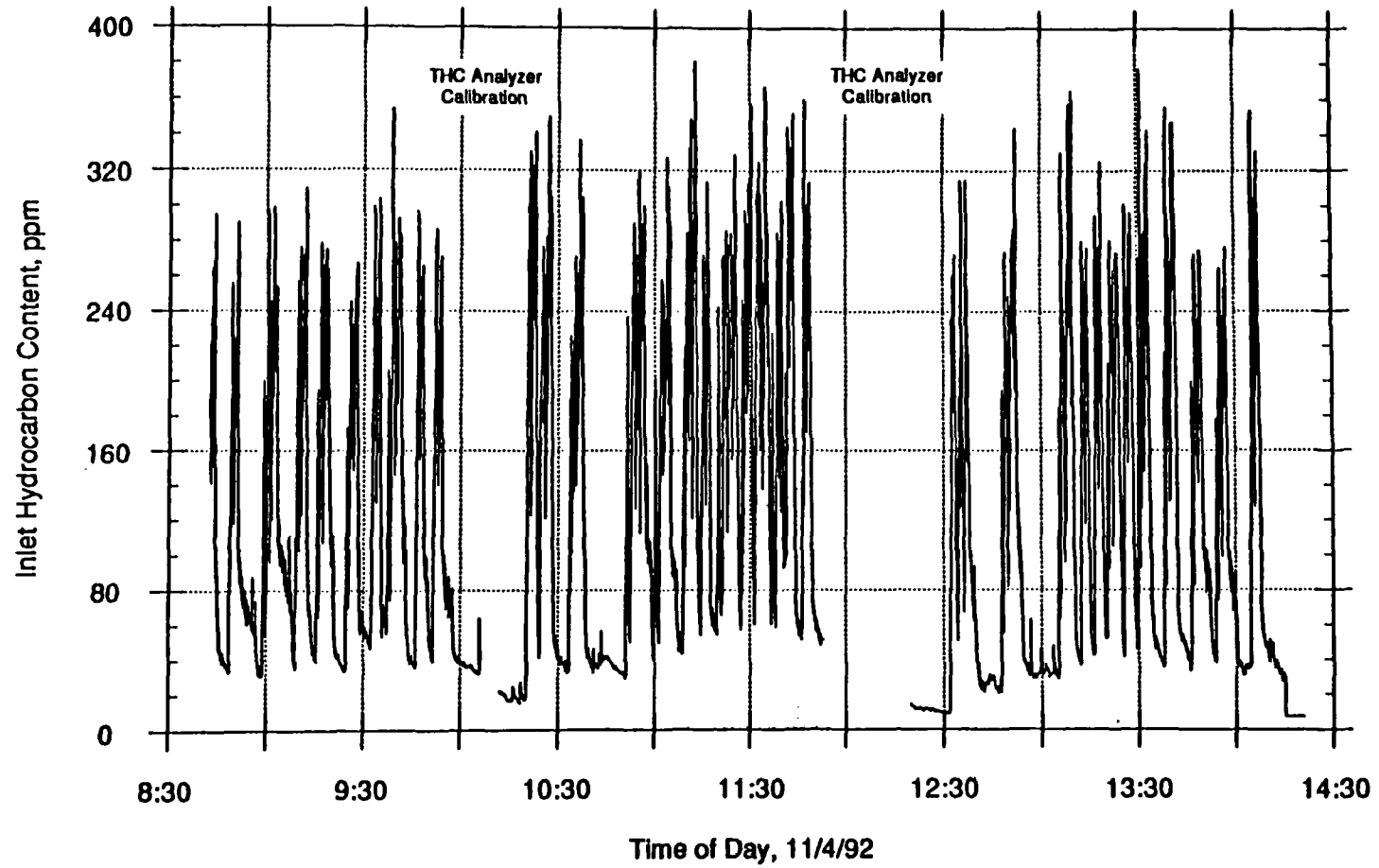


Figure 9. Inlet hydrocarbon emissions, November 4, 1992

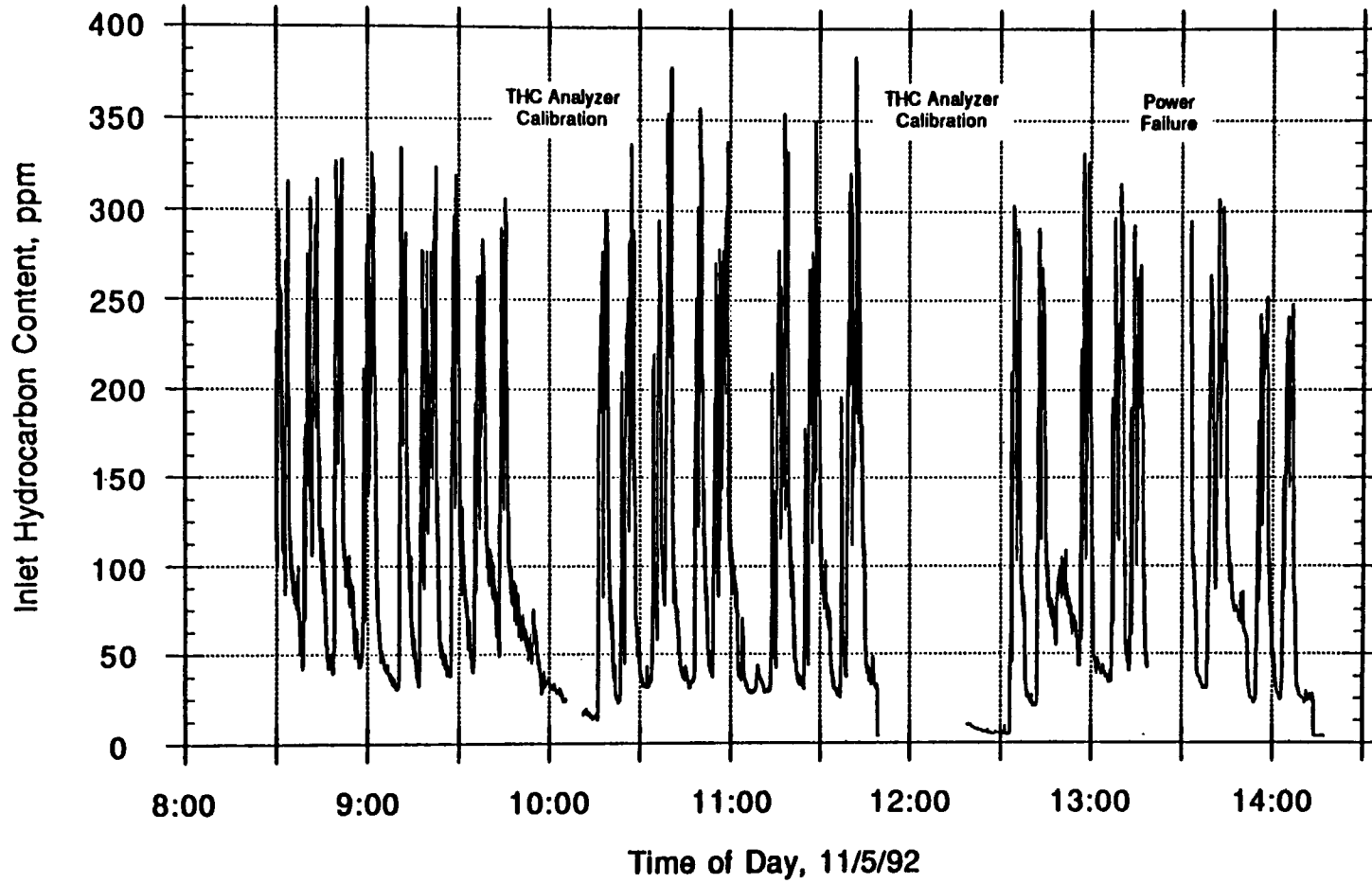


Figure 10. Inlet hydrocarbon emissions, November 5, 1992

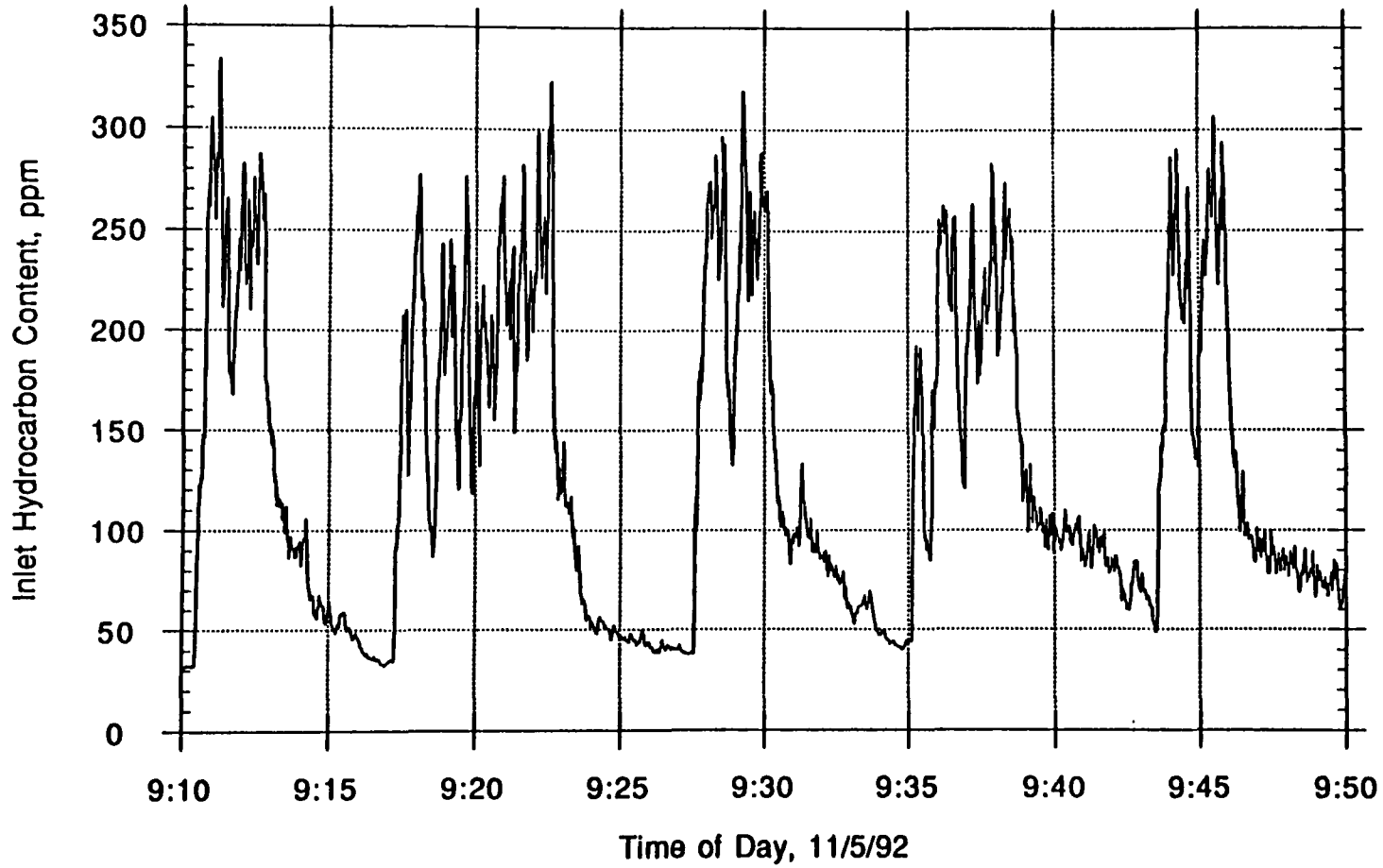


Figure 11. Inlet hydrocarbon emissions from 0910 to 0950, November 5, 1992

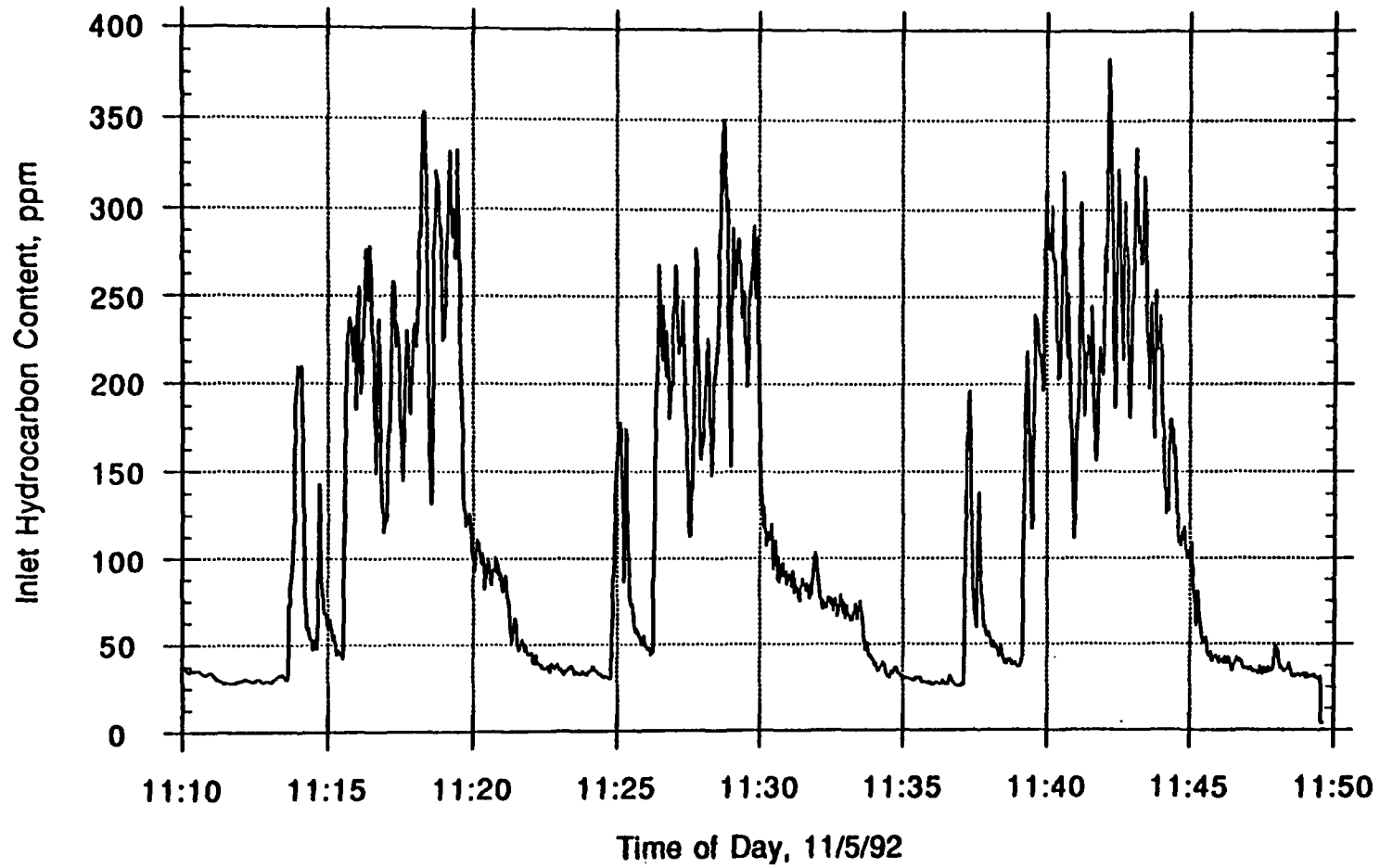


Figure 12. Inlet hydrocarbon emissions from 1110 to 1150, November 5, 1992

3.1.2 Outlet Data

Figures 13 through 15 show output from the outlet THC analyzer that was recorded on the datalogger for the three days of testing, November 3 through 5, 1992. As with THC data from the inlet, periods of calibration are not shown. Also not shown are data from periods when the FID in the outlet THC experienced a flame-out.

These data show that outlet emissions from the Polyad device are essentially uncoupled from inlet emissions. This behavior should be expected because the pilot-scale Polyad FB unit was designed to remove up to 1000 ppm of styrene before outlet emissions would be expected to increase. Thus, outlet emissions observed during this test were mainly due to the "bleeding" of solvent from Bonopore polymer that was not completely evolved in the desorption section.

Outlet emissions tended to decrease throughout the day. At the start of the test, 9 am on November 3, outlet emissions were near 22 ppm. Outlet emissions dropped to near 4.5 ppm after several hours and remained at that level for the balance of the day. On November 4, at the start of testing outlet emissions averaged nearly 15 ppm. During the day the emissions level dropped to about 6 ppm and thereafter increased slowly reaching approximately 8 ppm by the end of the day. This rise may have been due to the higher flow rate of Bonopore adsorbent used during that day (17 kg/h as opposed to 10 kg/h on other days). On November 5, the emissions level started out at approximately 7.5 ppm. However, at approximately 0925 outlet emissions were observed to rise quickly to about 11 ppm before they dropped back to about 5.5 ppm by 1030. The reason for this "spike" is not known because at that time the inlet emissions showed no such increase, as is shown in Figure 12. By the end of testing outlet emissions were in the range of 3 to 4 ppm.

The results shown in these figures are for total hydrocarbon emissions. Previous measurements (and other measurements to be reviewed here) have shown that virtually all of the VOC emissions from the Eljer facility occur as styrene. As indicated in Section 2.3.2, other VOC's were present in air at the outlet of the Polyad FB device because the device was contaminated with VOC residue from a previous test. However, because these contaminants did not contain styrene, it was possible to determine the portion of the outlet emissions that were due to styrene from analysis of the charcoal tube samples.

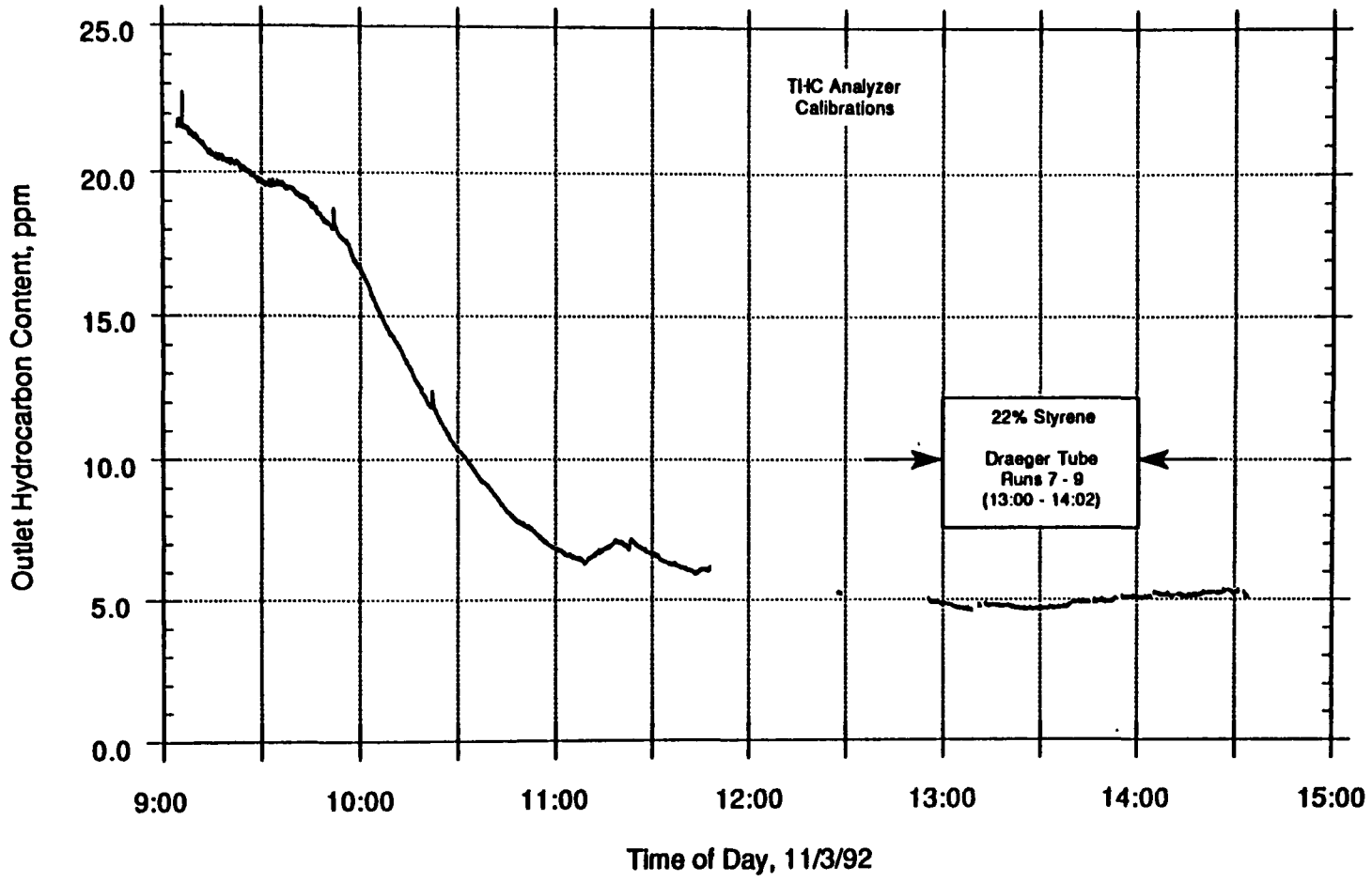


Figure 13. Outlet hydrocarbon emissions, November 3, 1992

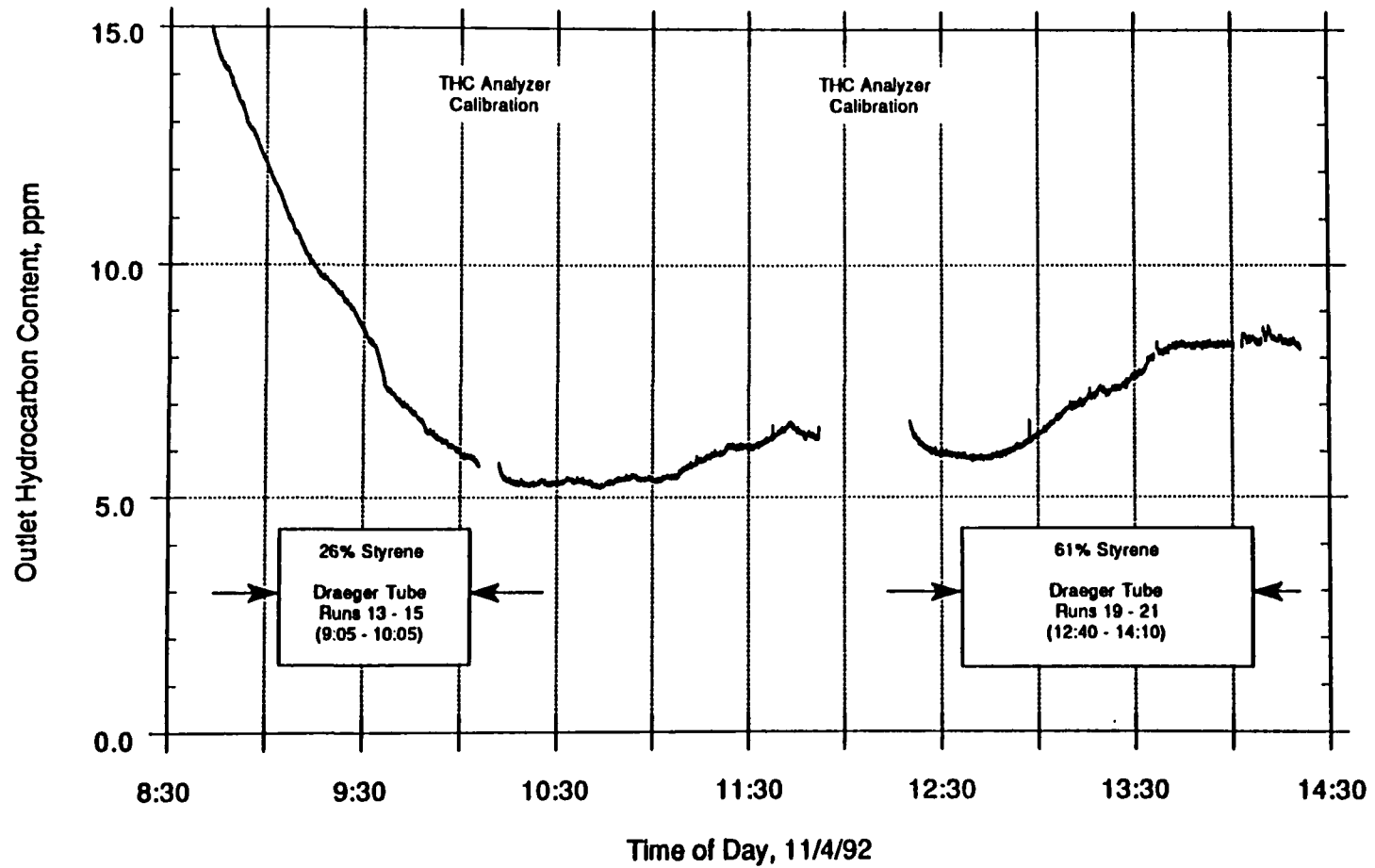


Figure 14. Outlet hydrocarbon emissions, November 4, 1992

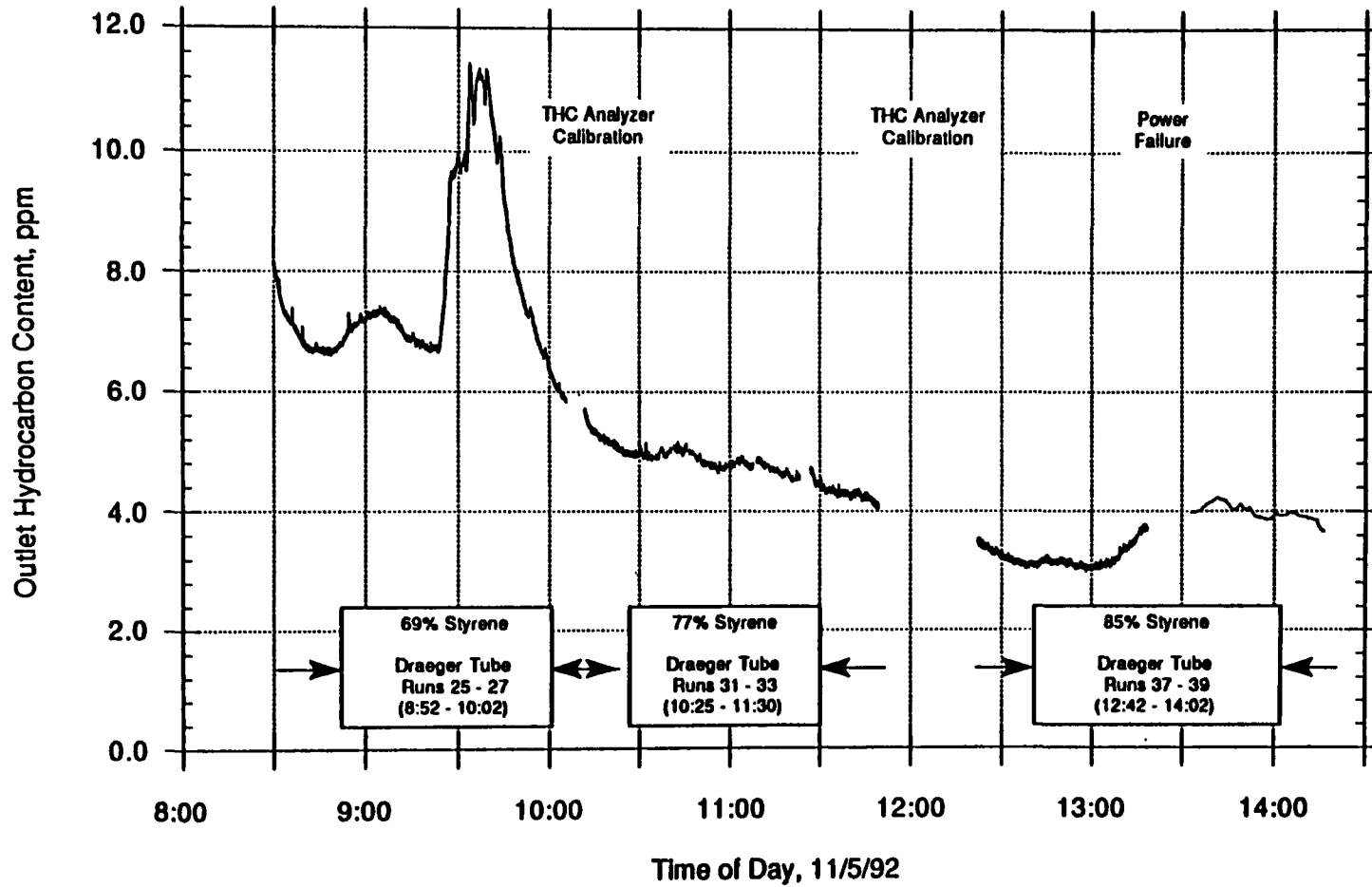


Figure 15. Outlet hydrocarbon emissions, November 5, 1992

Thus, in Figures 13 through 15, periods are shown during which charcoal tube (Draeger tube) samples were taken at the outlet of the Polyad device and the percentage of styrene measured in those samples is indicated on these figures. Taking into account the actual amount of styrene that was present at the outlet of the Polyad FB device, styrene emissions at the outlet of the Polyad FB device were never greater than 8 ppm. By the end of testing emissions of styrene had fallen to less than 4 ppm.

3.1.3 Efficiency Data

Figures 16 through 18 show calculated hydrocarbon penetration through the Polyad FB device and removal efficiency across the Polyad FB device for the three days of testing, November 3 through 5, 1992. Because of the cyclic nature of the inlet emissions the calculated penetration-efficiency curves shown in these figures exhibit the same cyclic nature. To provide the reader with visual information on average levels of penetration and efficiency over time so that trends can be seen, average penetration-efficiency values during each period of spraying are also shown in these figures along with curve fits through the peak average values during each period of spraying. As indicated above, outlet emissions appear to be essentially uncoupled from inlet emissions. Thus, the highest penetrations (lowest efficiencies) were observed during periods between sprayings and the lowest penetrations (highest efficiencies) were observed during periods of spraying. In terms of penetration-efficiency values measured during periods of spraying, efficiencies never fell below 91% and on the last day of testing an efficiency of over 99% was measured during one period of spraying at around 1300. Clearly, from the data collected during this period, the Polyad FB process was very efficient in collecting the styrene emissions.

Because of the rapid variability in process inlet emissions and the level of inlet emissions it was not possible to confirm the assertion made by Weatherly, Inc. that any stepwise increase in inlet emissions below 1000 ppm would not affect the immediate outlet emissions level for the Polyad FB pilot unit. However, the inlet and outlet emissions data presented above do suggest that within the levels of instantaneous emissions monitored at the inlet to the Polyad FB device (up to 400 ppm of styrene) outlet emissions are governed by "bleeding" of solvent from Bonopore polymer as it is reintroduced into the adsorber from the desorption section.

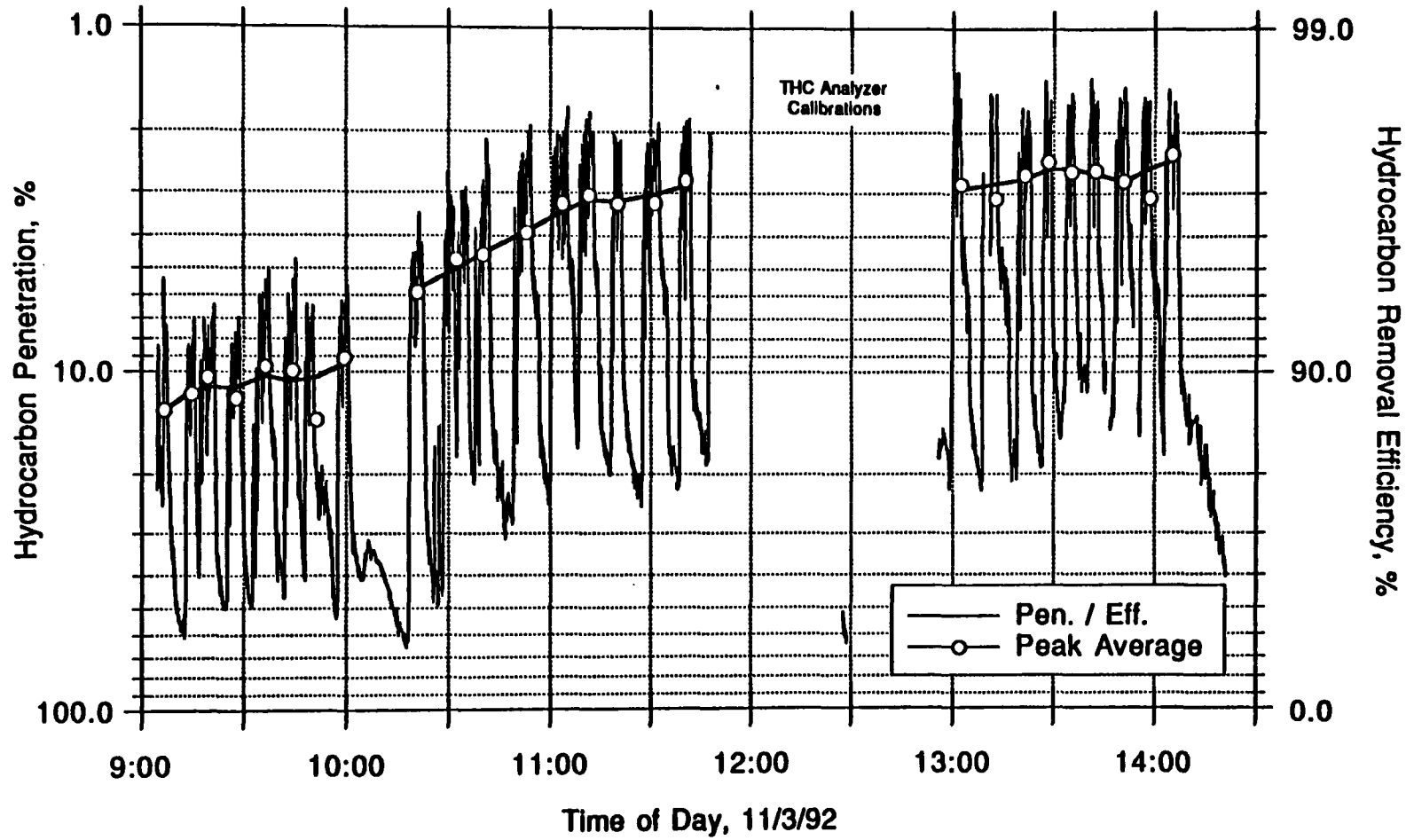


Figure 16. Hydrocarbon removal efficiency, November 3, 1992

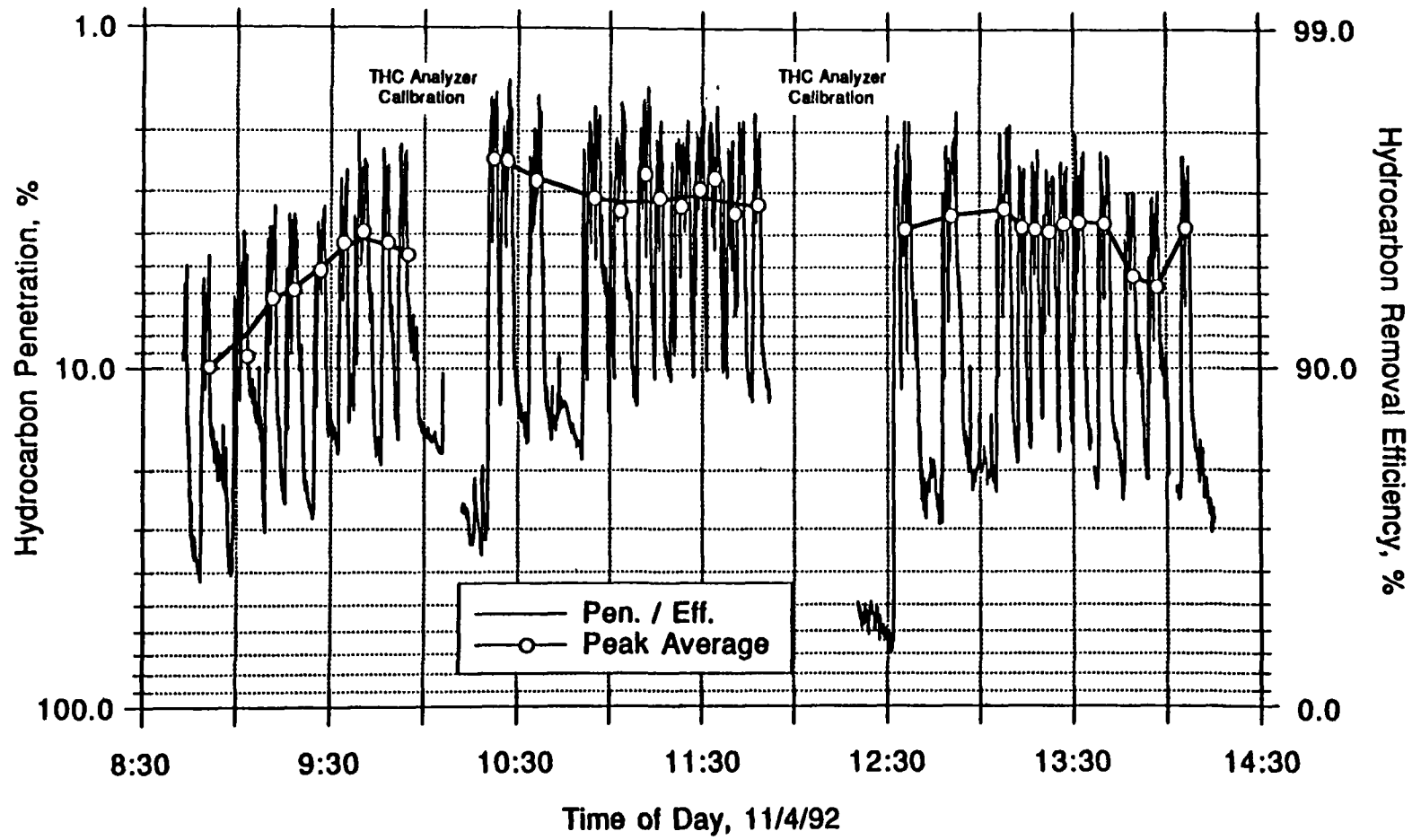


Figure 17. Hydrocarbon removal efficiency, November 4, 1992

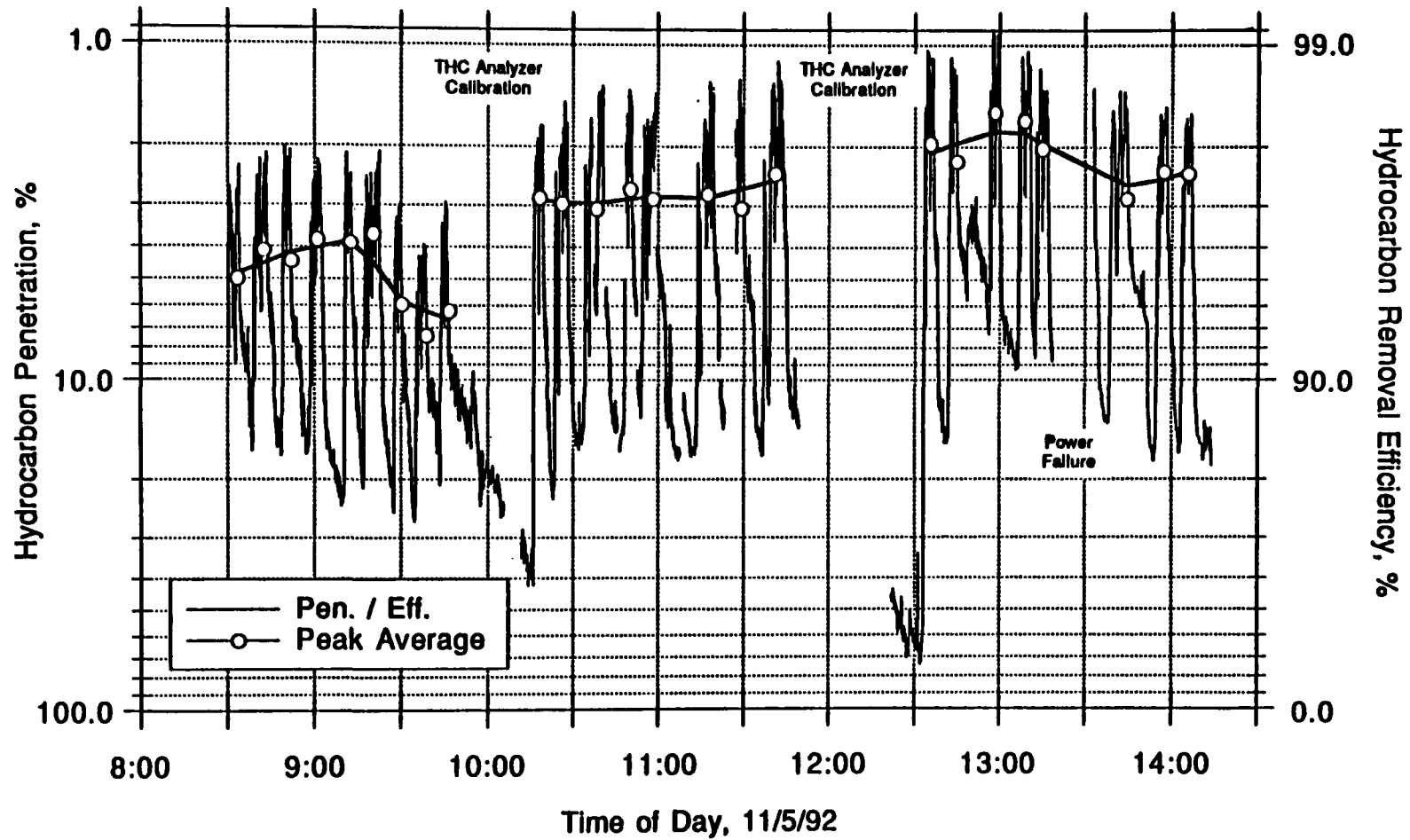


Figure 18. Hydrocarbon removal efficiency, November 5, 1992

Because outlet emissions were effectively not coupled to inlet emissions during this test it would be deceptive to concentrate on the relatively low penetration-efficiency values determined during periods between sprayings. Likewise, it may also be deceptive to concentrate on high penetration-efficiency values determined only during periods of spraying. Thus, in order to obtain a conservative estimate of the efficiency of the Polyad FB device the following approach was adopted: Inlet and outlet emissions were averaged during periods of spraying and during periods between sprayings. Penetrations and efficiencies were then calculated based on these averages. Overall averages were calculated for each of the three periods of active spraying for each day of testing and from these averages daily averages and a grand average of all the data were determined.

An inspection of the inlet emissions record suggested that an inlet hydrocarbon emissions level of 63 ppm was a reasonable cutoff point to determine if a mold was being sprayed. Thus, inlet emissions greater than 63 ppm were found to be typical for periods of spraying and inlet emissions of less than 63 ppm were found to be typical for periods between sprayings. THC data during each period of active spraying were averaged according to this criteria. Also, a record of the length of time of each spray/non-spray period was maintained as part of the averaging process. After averaging, the data were sorted by ascending emissions. Overall averages (weighted by the time span of each emission) were determined for periods when emissions were greater than 63 ppm and for periods when emissions were less than 63 ppm. Finally, the percentage of time that molds were sprayed was determined for each period of active spraying.

Table 2 shows the overall result of these calculations and includes the daily and grand test averages referred to above. Table 3 includes the averages for each of the three test daily periods of active spraying over the three days of testing. In these two tables no attempt was made to correct the level of outlet emissions for actual styrene content. Table 4 provides this correction for the times that the amount of styrene at the outlet was determined. In these tables average inlet and outlet emissions and efficiency and penetration are presented for periods when molds were sprayed (emissions > 63 ppm), between sprayings (emissions < 63 ppm) and for the entire period. Figures 19 and 20 present graphically the entire period averages shown in Tables 3 and 4 for each period of spraying. Tables

Table 2. Daily Averages and Grand Average of THC Analyzer Data,
November 3 through 5, 1992

1992 Date	Inlet Emissions Level	Percent of Time at that Level	Average Inlet THC ppm	Average Outlet THC ppm	Average Efficiency %	Average Penetration %
3 Nov	> 63 ppm	63.7	187.5	10.28	94.51	5.49
	< 63 ppm	36.3	39.2	9.10	76.79	23.21
	ALL	100.0	133.7	9.85	92.63	7.37
4 Nov	> 63 ppm	67.1	177.4	7.47	95.79	4.21
	< 63 ppm	32.9	41.7	7.31	82.47	17.53
	ALL	100.0	132.7	7.42	94.41	5.59
5 Nov	> 63 ppm	65.0	160.0	5.53	96.55	3.45
	< 63 ppm	35.0	40.4	5.21	87.10	12.90
	ALL	100.0	118.2	5.42	95.42	4.58
3 - 5 Nov	> 63 ppm	65.4	174.4	7.62	95.63	4.37
	< 63 ppm	34.6	40.5	7.13	82.37	17.63
	ALL	100.0	127.9	7.45	94.18	5.82

Table 3. Summary of THC Analyzer Data, November 3 through 5, 1992

1992 Date	Time Period for Spraying		Inlet Emissions Level	Percent of Time at that Level	Average Inlet THC ppm	Average Outlet THC ppm	Average Efficiency %	Average Penetration %
	Start	End						
3-Nov	9:04	10:01	> 63 ppm	71.8	173.7	19.40	88.83	11.17
			< 63 ppm	28.2	46.1	19.66	57.40	42.60
			ALL	100.0	137.7	19.47	85.86	14.14
	10:01	11:48	> 63 ppm	60.1	206.8	7.86	96.20	3.80
			< 63 ppm	39.9	38.7	7.64	80.28	19.72
			ALL	100.0	139.7	7.77	94.44	5.56
	12:54	14:21	> 63 ppm	61.8	176.9	4.81	97.28	2.72
			< 63 ppm	38.2	35.7	4.81	86.53	13.47
			ALL	100.0	122.9	4.81	96.09	3.91
4-Nov	8:42	10:05	> 63 ppm	71.4	152.6	9.69	93.65	6.35
			< 63 ppm	28.6	45.6	10.07	77.92	22.08
			ALL	100.0	122.0	9.80	91.97	8.03
	10:12	11:53	> 63 ppm	70.2	193.8	5.79	97.01	2.99
			< 63 ppm	29.8	44.4	5.53	87.56	12.44
			ALL	100.0	149.3	5.71	96.17	3.83
	12:19	14:15	> 63 ppm	60.6	182.0	7.30	95.99	4.01
			< 63 ppm	39.4	37.5	7.05	81.21	18.79
			ALL	100.0	125.0	7.20	94.25	5.75
5-Nov	8:29	10:05	> 63 ppm	69.5	156.5	7.97	94.91	5.09
			< 63 ppm	30.5	47.0	7.49	84.05	15.95
			ALL	100.0	123.1	7.82	93.65	6.35
	10:11	11:49	> 63 ppm	58.6	172.7	4.73	97.26	2.74
			< 63 ppm	41.4	37.6	4.78	87.28	12.72
			ALL	100.0	116.8	4.76	95.93	4.07
	12:19	14:14	> 63 ppm	67.3	151.6	3.57	97.65	2.35
			< 63 ppm	32.7	37.8	3.54	90.65	9.35
			ALL	100.0	114.4	3.56	96.89	3.11

Table 4. Styrene Removal from THC Data, November 3 through 5, 1992

1992 Date	Time Period for Spraying		Inlet Emissions Level	Percent of Time at that Level	Average Inlet THC ppm	Average Outlet THC ppm	Styrene in Outlet Air		Styrene Efficiency %	Styrene Penetration %
	Start	End					%	ppm		
3-Nov	12:54	14:21	> 63 ppm	61.8	176.9	4.81	21.8	1.05	99.41	0.59
			< 63 ppm	38.2	35.7	4.81	21.8	1.05	97.07	2.93
			ALL	100.0	122.9	4.81	21.8	1.05	99.15	0.85
4-Nov	8:42	10:05	> 63 ppm	71.4	152.6	9.69	26.2	2.54	98.34	1.66
			< 63 ppm	28.6	45.6	10.07	26.2	2.64	94.22	5.78
			ALL	100.0	122.0	9.80	26.2	2.57	97.90	2.10
	12:19	14:15	> 63 ppm	60.6	182.0	7.30	61.5	4.48	97.54	2.46
			< 63 ppm	39.4	37.5	7.05	61.5	4.33	88.45	11.55
			ALL	100.0	125.0	7.20	61.5	4.42	96.46	3.54
5-Nov	8:29	10:05	> 63 ppm	69.5	156.5	7.97	69.3	5.53	96.47	3.53
			< 63 ppm	30.5	47.0	7.49	69.3	5.19	88.95	11.05
			ALL	100.0	123.1	7.82	69.3	5.43	95.60	4.40
	10:11	11:49	> 63 ppm	58.6	172.7	4.73	77.2	3.66	97.89	2.11
			< 63 ppm	41.4	37.6	4.78	77.2	3.69	90.17	9.83
			ALL	100.0	116.8	4.76	77.2	3.67	96.86	3.14
12:19	14:14	> 63 ppm	67.3	151.6	3.57	84.8	3.03	98.00	2.00	
		< 63 ppm	32.7	37.8	3.54	84.8	3.00	92.07	7.93	
		ALL	100.0	114.4	3.56	84.8	3.02	97.36	2.64	

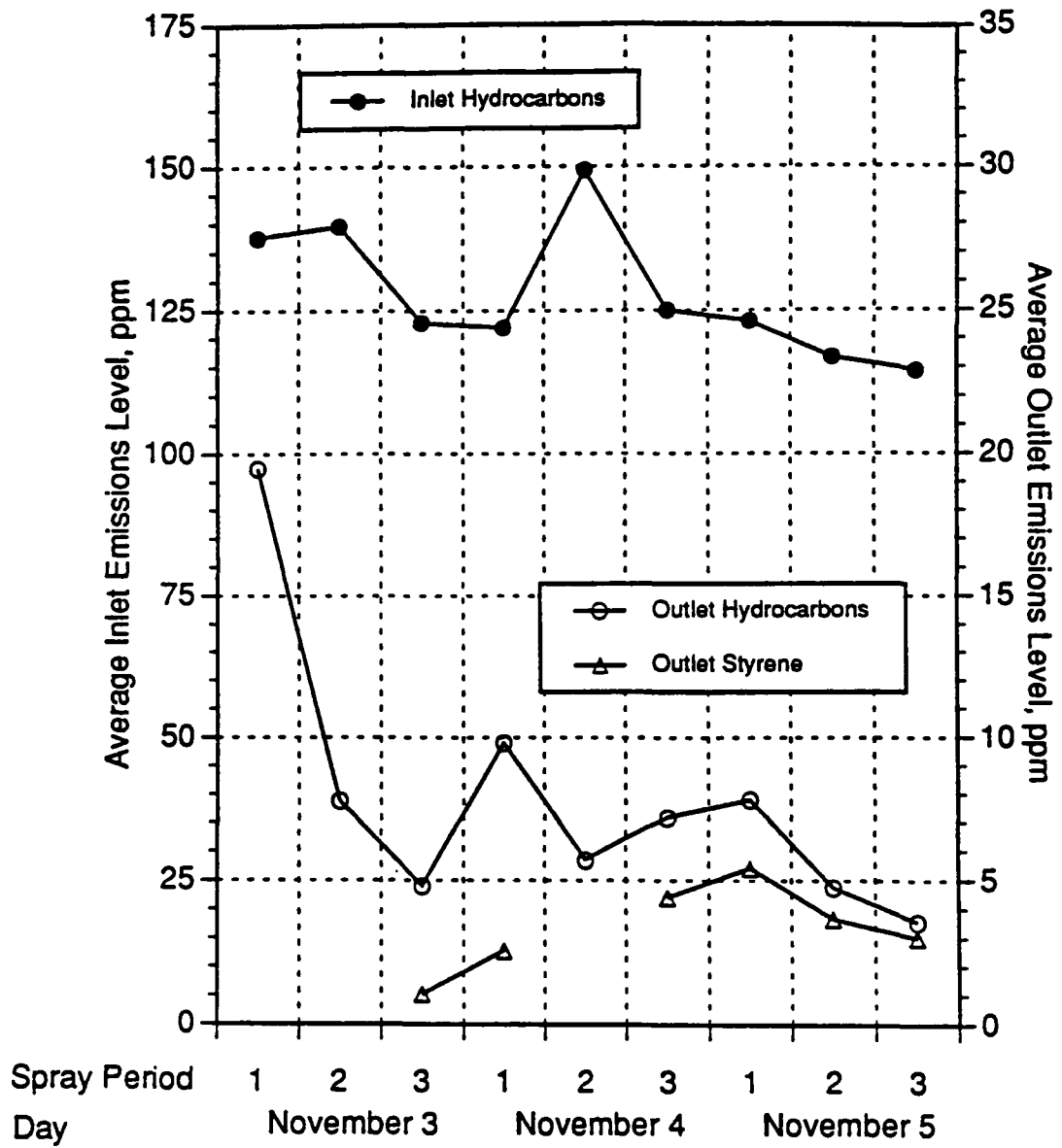


Figure 19. Average inlet and outlet hydrocarbon and styrene emissions for each period of spraying

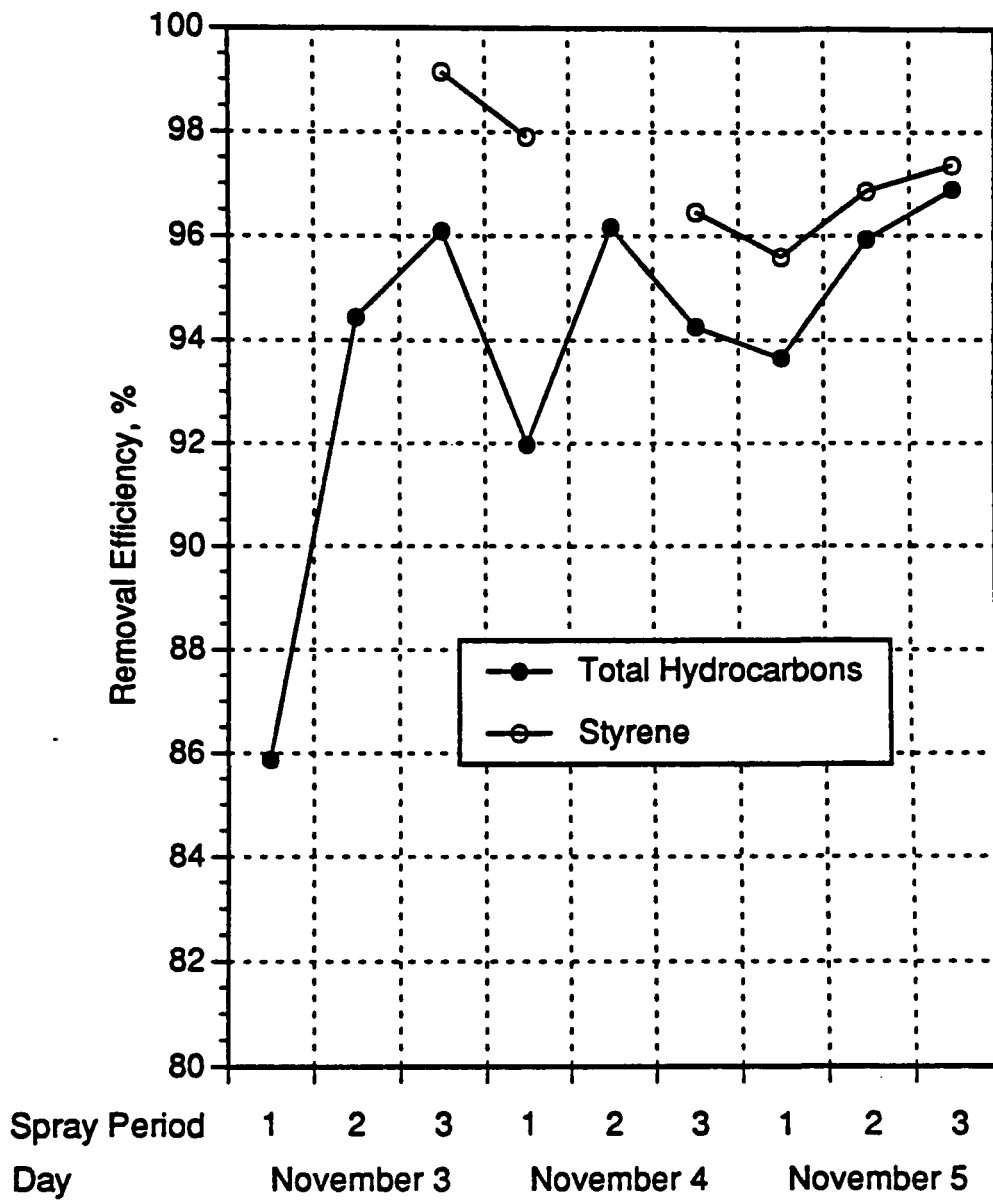


Figure 20. Average hydrocarbon and styrene removal efficiency for each period of spraying

detailing averages within each period of active spraying (sorted by time) along with population standard deviations and 95% confidence intervals are presented in Appendix C.

Tables 2 and 3 show that, on the average, 65% of each period of active spraying activity is occupied by spraying. During these periods the average level of styrene emissions at the inlet ranged from 152 to 207 ppm while the average level of hydrocarbon emissions at the outlet ranged from 3.6 to 9.8 ppm (excluding the first period of active spraying on November 3). If the first period of active spraying on November 3 is excluded the average efficiency during periods of spraying ranged from 93 to nearly 98%, and the average efficiency during periods between sprayings ranged from 78 to almost 91%. Overall, an average efficiency of just slightly greater than 94% was measured for the test.

Table 4 and Figure 19 show that styrene at the outlet increased before it started to decrease. These data also show that outlet emissions dropped by a factor of over four from the beginning to the end of the test. This is probably because during most of the first two days of testing outlet emissions were dominated by the evolution of naphthalene-related contaminants from the Bonopore polymer.

If data from the last period of the last day of testing can be viewed as representative of the Polyad FB process (in the absence of contamination) then, as Table 4 and Figure 20 show, overall efficiencies of at least 97% can be achieved.

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 Polyad FB device. 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 mg of styrene per m³/s of air flow. This value was multiplied by the nominal flow rate of the vent exhaust fan (6.84 m³/s or 14,500 cfm) to obtain a mass emissions rate of styrene to the atmosphere for each bath tub or shower stall.

Table 5 shows the results of these calculations with population standard deviations and 95% confidence intervals. Over the three days of testing sufficient data were acquired to estimate styrene

Table 5. Summary of Estimated Styrene Emissions from Gel Coat Booth #2, THC Data

Date	Start	End	Units Sprayed	-----Time to Spray Each Unit -----			-- Styrene Emissions per Unit --		
				Average (sec)	Pop. Std. Dev. (sec)	95% C. I. (sec)	Average (kg)	Pop. Std. Dev. (kg)	95% C.I. (kg)
3-Nov	9:04	10:01	8	304.5	58.9	40.8	1.551	0.296	0.205
	10:18	11:42	9	356.6	93.8	61.3	2.137	0.530	0.346
	12:59	14:07	9	297.6	81.1	53.0	1.521	0.318	0.208
	Daily Summary		26	320.1	84.2	32.4	1.744	0.492	0.189
4-Nov	8:48	9:57	9	322	99.1	64.7	1.470	0.353	0.231
	10:20	11:50	12	328.7	99.2	56.1	1.842	0.448	0.254
	12:32	14:08	12	290.8	81.5	46.1	1.541	0.315	0.178
	Daily Summary		33	313.1	94.7	32.3	1.631	0.411	0.140
5-Nov	8:29	9:49	9	373.7	68.8	44.9	1.761	0.274	0.179
	10:16	11:45	8	410.1	108.7	75.3	1.990	0.460	0.319
	12:33	14:07	8	340.9	146.7	101.6	1.619	0.547	0.379
	Daily Summary		25	374.8	114.6	44.9	1.789	0.462	0.181
3-5 Nov	Test Summary		84	333.6	101.8	21.8	1.713	0.458	0.097

mass emissions for a total of 91 separate mold sprayings. On the average, 5.6 ± 1.7 minutes were required to spray a mold and during that time approximately 1.9 ± 0.5 kg of styrene was vented to the atmosphere, assuming that the exhaust fan in gel coat booth #2 was operated at its nominal flow rate. The fairly high population standard deviations for these numbers are most likely due to the fact that two different types molds were sprayed and that bath tub enclosures require a longer time to spray (with higher emissions) than smaller shower stalls.

3.2 VOLATILE ORGANIC COMPOUND DATA

NIOSH Method 1501 (equivalent to EPA Method 18, Adsorption Tube Procedure) was followed to obtain charcoal tube samples at selected booth exhausts and at the inlet and outlet of the Polyad FB device situated at gel coat booth #2. Due to the nature of the adsorption tube sampling procedure and the desire to sample process emissions over an extended period, sample times of from one to one and one-half hours were typical.

During a pretest visit on October 13, 1992 charcoal tube samples were obtained at the roof exhaust stack of gel coat booth #2. Later, on November 6, 1992, charcoal tube samples were obtained at the roof exhaust stack of first lay-up booth #5 and second lay-up booth # 7. As described above, during each day of sampling from November 3 -5, 1992 charcoal tube samples were obtained from air exhausted from gel coat booth #2 (the inlet of the Polyad FB device) and air exhausted from the Polyad FB device.

Only one operational problem was encountered during this testing. This was when a 15 minute power failure occurred on the last day of sampling. Even though the battery-powered pumps that were used to acquire these samples continued to function during the interval while power was lost, the sample bypass pumps did not operate during that time (19% of the 80 minute sample period). Thus, those particular samples may not be completely representative of the process.

Equipment problems did significantly affect sampling. After testing was completed it was discovered that both sample pumps did not maintain proper sample flow under negative inlet pressures typical of those found during this test (approximately 1 kPa above that required to sample through the sample manifold with three charcoal tubes attached). These pumps are designed to maintain flow at

negative inlet pressures of up to 10 kPa (40 in H₂O). This problem was exacerbated by a crack in the tube of the Gilian Instruments flow calibrator that prevented it from being operated at a negative pressure of more than 0.25 kPa (1 in. H₂O). Thus, although the sample pumps were calibrated before each use, they could not be calibrated with the flow calibrator inserted into the sample line before each charcoal tube. The net effect of this was to render the charcoal tube data taken from November 3 - 5, 1992 unusable except for information as to styrene content. Fortunately, charcoal tube samples taken at roof exhaust vents during the pretest visit on October 12 and after testing was completed on November 6 were usable because for these measurements the sample pumps were calibrated for flow under the actual conditions of use.

3.2.1 Measurements at Spray Booth Exhaust Stacks

Charcoal tube samples were obtained at the exhaust stack of gel coat booth #2 during the pretest visit on October 13, 1992. Samples were also taken at the exhaust stack of first lay-up booth #5 and second lay-up booth # 7 on November 6, 1992. While samples taken at the outlet of other types of spray booths were not required to determine the applicability of the Polyad FB device to controlling styrene emissions from a gel-coating booth, these measurements were necessary to determine if styrene emissions from the gel-coating operation were characteristic of other parts of the bath tub and shower stall manufacturing process. Also, if higher levels of styrene emissions were typical of other parts of the manufacturing process, costs to install and maintain a Polyad FB - type of control device would be affected. Tables 6 and 7 summarize the results of these measurements.

Table 6 presents the sample parameters, spraying times, and number of units sprayed during each set of runs and Table 7 presents averages with population standard deviations, emissions levels of styrene in ppm, and emission rate in kg of styrene per hour and kg of styrene per unit sprayed. Because the number of molds sprayed were recorded during each period of sampling, it was possible to determine an emission rate in terms of the amount of styrene emitted to the atmosphere per mold sprayed. Compared to styrene emissions rates reported in Table 5 for gel coat booth #2 on November 3 - 5, the level of styrene emissions measured on October 13 with charcoal sample tubes are lower. However, on October 13, at gel coat booth #2 only 44% of the time was spent in spraying (each period

Table 6. Sampling Conditions for Measurements made at the Outlet of Gel Coat Booth #2, First Lay-Up Booth # 5, and Second Lay-Up Booth #7, October - November, 1992. EPA Method 18/NIOSH Method 1501 Sampling.

Date	Location	Sample Numbers	Start Time	End Time	Sample Time min	Time Spent Spraying		Number of Units Sprayed	Average Time to Spray a Mold sec
						min	%		
10/13	Gel Coat Booth #2	1 - 6	13:10	14:14	64	28.17	44.0	8	211.9 ± 36.7
11/6	First Lay-Up Booth #5	40 - 42	08:40	09:40	60	21.08	35.1	15	84.3 ± 26.9
	Second Lay-Up Booth #7	43 - 45	08:40	09:40	60	28.33	47.2	27	63.0 ± 20.1

Table 7. Styrene Concentrations Measured at the Outlet of Gel Coat Booth #2, First Lay-Up Booth # 5, and Second Lay-Up Booth #7, October - November, 1992. EPA Method 18/NIOSH Method 1501 Sampling.

Date	Location	Sample Number	Sample Volume liters	Styrene Measured μg	Styrene Concentration ppm	Equivalent Styrene Emissions		Styrene Measured %
						kg/h	kg/Unit	
10/13	GC #2	1*	16.09	141.4	2.1	0.22	0.029	>99
		2	13.68	6154.3	105.7	11.08	1.478	>99
		3	16.69	6702.7	94.3	9.89	1.319	>99
		4	13.41	6071.6	106.3	11.15	1.487	>99
		5	14.13	6102.1	101.4	10.64	1.419	>99
		6	13.97	5965.5	100.3	10.52	1.403	>99
	Average**				101.6 \pm 4.3	10.66 \pm 0.45	1.421 \pm 0.061	N/A
11/6	FLU #5	40	16.08	5664.6	84.3	8.68	0.579	99.76
		41	15.52	5853.9	90.2	9.29	0.619	99.69
		42	15.94	5544.7	83.2	8.57	0.571	99.65
	Average				85.9 \pm 3.1	8.85 \pm 0.32	0.590 \pm 0.021	99.70 \pm 0.05
	SLU #7	43	7.08	3611.5	122.3	12.57	0.465	99.66
		44	6.64	3138.5	113.4	11.65	0.431	99.77
45		7.00	4359.2	149.1	15.34	0.568	99.82	
Average				128.3 \pm 15.2	13.18 \pm 1.57	0.448 \pm 0.017	99.72 \pm 0.05	

* Not representative, leak around tube

** Sample #1 not in averages or population standard deviations

of spraying averaged 212 seconds). As Tables 2 and 5 show, during November, molds were usually sprayed for 65% of any period of spraying activity and the average period of spraying was approximately 334 seconds long. Thus, styrene emissions measured for October 13 may be less than those measured during November because of a lower production rate.

For styrene emissions measured at first lay-up booth #5 and second lay-up booth #7 exhaust vents on November 6, production rates were higher and styrene emission rates per unit were lower than that observed for the gel coating operation at any time. In first lay-up booth #5, 15 units were sprayed over an hour of sampling (84 seconds of spraying per unit) with an average emission rate of 0.59 kg/unit sprayed. At second lay-up booth #7, 27 units were sprayed over an hour of sampling (63 seconds of spraying per unit) with an average emission rate of 0.45 kg/unit sprayed. Evidently the second and third stages of manufacture require shorter times to complete than does the initial stage of spraying with gel coat. Also, as Table 6 shows, the population standard deviation for average time to spray a unit can be large compared to the average. These large standard deviations are almost certainly due to the mix of units sprayed (bath tubs and shower stalls with different surface areas).

On a per unit basis, styrene emissions are lower for the last two stages of manufacture which might be expected because the mix sprayed in these last two processes contains less styrene monomer than the mix sprayed in the gel coating process. However, on an hourly basis, at second lay up booth #7, styrene emissions were greater than measured at gel coat booth #2 (13.2 kg/h versus 10.7 for gel coat booth #2 and 8.9 kg/h for first lay-up booth #5).

Compared with the results from THC measurements reported in Table 2, mass emissions measured for first lay-up booth #5 (86 ppm) and gel coat booth #2 (102 ppm) appear very low compared to the average for all spraying at gel coat booth #2 (128 ppm, Table 2) while mass emissions measured for second lay-up booth #7 (128 ppm) agree better. In terms of emissions of styrene per unit sprayed, the results from gel coat booth #2 from October 13, (1.42 kg/unit) agree better with the result shown in Table 5 (1.71 kg/unit), especially when the time of spraying is taken into account (6.7 g/sec on October 13 versus 5.1 g/sec for November 3-5).

With respect to the amount of styrene present in the samples, while it was only verified for the samples taken in October that styrene was the only significant VOC present in emissions from gel coat booth #2, quantitative determination of styrene was performed for the samples taken in November. As Table 6 shows, styrene is essentially the only VOC present in the booth exhaust air at the Eljer facility.

3.2.2 Measurements at the Inlet and Outlet of the Polyad FB Device

Table 8 summarizes the results of measurements made at the inlet of the Polyad FB device and Table 9 summarizes the results of measurements made at the outlet of the Polyad FB device during testing on November 3-5, 1992. Because of the sampling problems discussed above, Tables 8 and 9 show the percentage of styrene and amount of styrene collected rather than concentration of styrene measured. Tables 8 and 9 also include averages and population standard deviations for each triplicate set of runs.

Table 8 shows the amount of styrene at the inlet of the Polyad FB device from November 3 to November 5. This table also shows the percentage of styrene measured at the inlet as compared to the total amount of material detected. While these numbers do not indicate as high a percentage of styrene in the exhaust of gel coat booth #2 as was reported in Table 7, an inspection of the gas chromatograms for each sample shown in Table 8 suggests that the samples were not contaminated by any particular compound. These results also show the effects of the malfunctioning of the sample pump. The third sample in each set usually has much less styrene present than is present in the first two samples.

Table 9 presents the amount of styrene at the outlet of the Polyad FB device from November 3 to November 5 and clearly shows that the amount of styrene in the gas exiting the Polyad FB device increased throughout the test. This was probably due to the desorption of naphthalene-related contaminants from previous testing with the Polyad FB pilot unit (see Section 2.3.2). These samples also show the effects of a malfunctioning sample pump. The effect was probably more drastic at the outlet, compared to the inlet, because a higher sample flow rate was used. Flow through the third tube in each manifold was very low and so little styrene was detected that it cannot be assumed that the amount of styrene present was reliably measured. Therefore, these samples were excluded from condition averages and population standard deviations.

Table 8. Results of EPA Method 18/NIOSH Method 1501
 Samples Taken at the Inlet of the Polyad FB
 Device , November 3 to November 5, 1992

Date	Run Number	Start Time	End Time	Styrene %	Styrene μg	Average Styrene, %*
11/3	1	10:26	11:26	96.47	1563.1	96.89 \pm 0.34
	2			96.91	4123.8	
	3			97.30	6072.0	
11/3	4	13:00	14:02	97.96	4909.2	97.39 \pm 0.49
	5			97.46	1899.4	
	6			96.76	120.4	
11/4	10	9:05	10:05	97.32	5043.3	97.47 \pm 0.53
	11			96.91	1149.6	
	12			98.19	33.0	
11/4	16	12:40	14:10	97.34	7614.2	96.04 \pm 1.58
	17			96.96	4019.4	
	18			93.81	80.4	
11/5	22	8:52	10:02	97.39	5979.9	97.68 \pm 0.78
	23			96.91	1863.7	
	24			98.75	50.7	
11/5	28	10:25	11:30	97.26	4332.2	97.14 \pm 0.09
	29			97.04	1917.4	
	30			97.14	38.5	
11/5	34	12:42	14:02	97.26	6988.4	96.07 \pm 1.31
	35			96.71	2708.9	
	36			94.24	105.1	

* \pm one population standard deviation

**Table 9. Results of EPA Method 18/NIOSH Method 1501
Samples Taken at the Outlet of the Polyad FB
Device , November 3 to November 5, 1992**

Date	Run Number	Start Time	End Time	Styrene %	Styrene μ g	Average Styrene, %*
11/3	7	13:00	14:02	17.67	31.9	21.75 \pm 4.08
	8			25.83	38.8	
	9**			27.69	3.4	
11/4	13	9:05	10:05	21.78	103.5	26.19 \pm 4.42
	14			30.61	117.8	
	15**			41.29	5.1	
11/4	19	12:40	14:10	61.52	282.1	61.45 \pm 0.06
	20			61.39	324.5	
	21†			97.32	78.2	
11/5	25	8:52	10:02	69.22	210.1	69.32 \pm 0.10
	26			69.42	158.0	
	27**			36.55	7.2	
11/5	31	10:25	11:30	81.12	205.7	77.22 \pm 3.90
	32			73.32	181.5	
	33**			48.78	7.3	
11/5	37	12:42	14:02	85.87	212.8	84.83 \pm 1.04
	38			83.78	184.0	
	39**			52.72	11.3	

* \pm one population standard deviation

** Too little sample for accurate determination, excluded from average and population standard deviation

† Inconsistent result and small styrene sample, excluded from average and population standard deviation

3.3 Analysis of Recovered Solvent Sample

After testing had ended on November 5, the solvent recovery unit in the Polyad FB device was drained and 2600 ml of liquid was recovered. This liquid had a strong odor, different from that of styrene. Approximately 100 ml of this liquid was preserved in a glass container with a Teflon sealed cap and transported to Birmingham for analysis.

A sample of the liquid was diluted with carbon disulfide (1:100) and subjected to GC-FID analysis to determine styrene content. It was determined that styrene was present in the sample and was the largest constituent, but only at a concentration of 28.7 %. Many other hydrocarbons were present. A second sample of the liquid was subjected to GC analysis with mass spectrographic detection to identify what compounds were present. An NBS-certified software library was used for compound identification. Table 10 presents the results of this analysis.

As Table 10 shows, only two compounds could not be identified. The compounds other than styrene appear to be contamination from the Polyad FB unit. As noted above, before being evaluated at Eljer Plumbingware, the Polyad FB unit had been tested at a chemical plant that produced naphthalene. The sample recovery reservoir in the Polyad FB unit was not drained at the end of that test. When the Polyad FB unit was prepared for this test, the reservoir was not drained nor was the Bonopore adsorbent changed. Thus, naphthalene and naphthalene-related VOC's were present in the Polyad FB unit at the start of the test and throughout the test they continued to be desorbed from the Bonopore adsorbent.

3.4 Total Flow Rate Data

Following the methodology described in Section 2.5.4, air flow into the Polyad FB device was measured during each day of testing. Table 11 presents the results of these measurements. The flow measurements made on November 3 (at 14:45) and November (at 08:55) 5 were the actual flows used for testing. On November 4, flow rate measurements were made at the end of the day (14:45). The flow rate indicated as "Flow for Testing" in Table 11 was the flow rate used during that day. Flow rates were measured at two other fan settings to help determine the fan setting to be used for the final day of testing.

Table 10. Compounds Identified in Liquid Sample Recovered from the Polyad FB Device

Compound Identified*	Percent Present	Amount (ml)
Unknown - 1	1.439	37.4
Styrene	25.737	669.2
Unknown - 2	4.578	119.0
Diethyl Benzene	17.028	442.7
1,2 - Diethyl Benzene	16.052	417.4
1,3 - Diethyl Benzene	5.071	131.9
2 - Methyl - 2 - Propenyl Benzene	5.809	151.0
Naphthalene	17.342	450.9
Bis (2 - Ethylhexyl) Phthalate	6.944	180.5
Total of Compounds Present	100.000	2600.0

Table 11. Flow Rate Measurements at the Inlet of the Polyad FB Device

Date and Time	Distance from Far Wall of Duct* cm	First Traverse m/min	Second Traverse m/min	Average Velocity m/min	Average Flow Rate** m ³ /min
11/3/92, 14:45	1.3	259.1	N/A	259.1	4.47 ± 0.38
	3.8	289.6	N/A	289.6	
	6.4	266.7	N/A	266.7	
	8.9	228.6	N/A	228.6	
	11.4	289.6	N/A	289.6	
Average				266.7 ± 22.6	
11/4/92, 14:45 (Flow for testing)	1.3	266.7	281.9	274.3	4.81 ± 0.28
	3.8	304.8	320.0	312.4	
	6.4	274.3	289.6	281.9	
	8.9	259.1	274.3	266.7	
	11.4	292.6	304.8	298.7	
Average				286.8 ± 16.6	
(Trial Flow #1)	1.3	350.5	335.3	342.9	5.78 ± 0.37
	3.8	373.4	373.4	373.4	
	6.4	342.9	335.3	339.1	
	8.9	304.8	312.4	308.6	
	11.4	358.1	365.8	362.0	
Average				345.2 ± 22.2	
(Trial Flow #2)	1.3	388.6	381.0	384.8	6.12 ± 0.36
	3.8	396.2	373.4	384.8	
	6.4	359.7	335.3	347.5	
	8.9	335.3	329.2	332.2	
	11.4	381.0	373.4	377.2	
Average				365.3 ± 21.5	
11/5/92, 08:55	1.3	365.8	350.5	358.1	5.63 ± 0.38
	3.8	335.3	365.8	350.5	
	6.4	312.4	312.4	312.4	
	8.9	304.8	304.8	304.8	
	11.4	358.1	350.5	354.3	
Average				336.0 ± 22.7	

* The duct diameter was 14.61 cm

** The flow rate used for testing appears in bold face type.

3.5 Styrene Captured by the Polyad FB Device

Using the flow measured during each day of testing and the total time of spraying, it is possible to estimate the minimum amount of air that passed through the Polyad FB device while styrene was present. Also, if it is assumed that 95% of the styrene that entered the Polyad FB unit was captured and completely recovered from the Bonopore adsorbent and that the average level of styrene present in the exhaust air from gel coat booth #2 during periods of spraying was 128 ppm (from Table 2), then it is possible to estimate the maximum amount of styrene that should have been recovered by the Polyad FB device. Table 12 shows that amount to be 1.9 kg or 2.1 liters of liquid styrene.

Unfortunately, it is not possible to reconcile the amount of styrene that should have been recovered with the amount of styrene that was recovered. This is because after testing had been completed on November 4 (from 15:00 until 18:30 when the unit was powered down), and before testing was started on November 5 (from 07:00 when the unit was powered up until 08:50), the return air line from the desorber was vented to the atmosphere (as recorded in the Weatherly, Inc. Polyad Mobile Unit Log Book for the test at the Eljer Facility). The reason given in the Log Book for this modification to the device was: "To remove residual sorbent from previous testing." Thus, an unknown amount of styrene that would have been otherwise recovered was lost.

However, if even half of the styrene that could have been collected through the whole test was lost, approximately 500 ml of styrene liquid would remain unaccounted for. Two explanations are possible. First, some styrene did remain on the Bonopore adsorbent at the end of the test. A sample of the Bonopore adsorbent sent to SRI after the test retained a strong, styrene-like odor. Second, because the recovered solvent container in the Polyad FB device is not designed to be completely emptied, some condensed liquid may not have been recovered.

Table 12. Estimated Styrene Capture in the Polyad FB Device

Date	Spraying Start/Stop Times	Polyad FB Operation hours	Polyad FB Flow Rate m ³ /min	Volume of Air Sampled m ³	Estimate of Styrene Recovered* Liters
11/3	09:04 - 10:01	0.95	4.47	978.9	0.58
	10:01 - 11:48	1.49			
	12:54 - 14:21	1.21			
11/4	08:42 - 10:05	1.25	4.81	1301.6	0.76
	10:12 - 11:53	1.54			
	12:19 - 14:15	1.72			
11/5	08:29 - 10:05	1.42	5.63	1462.7	0.76
	10:11 - 11:49	1.48			
	12:19 - 14:14	1.43			
Total		12.49		3743.2	2.10

* Assuming daily average styrene concentrations from Table 2 and a liquid styrene density of 0.9074 g/ml

SECTION 4
COSTS ASSOCIATED WITH APPLYING THE POLYAD FB SYSTEM
TO STYRENE REMOVAL

In terms of styrene removal, the mobile Polyad FB pilot unit exhibited excellent performance. Based on the results of this evaluation, this technology can be expected to easily meet or exceed a 95% average removal efficiency for styrene entrained in air. While such performance is excellent, this technology is only suitable if it can compete with other styrene removal technologies on a cost basis. Thus, Weatherly, Inc. was asked to provide a price quote for a Polyad FB system suitable for the Eljer facility.

Price quotes were obtained for two Polyad systems. The first system corresponds to the configuration tested at Eljer Plumbingware: an adsorber/desorber system with solvent recovery (the Polyad Recovery System). The second system incorporates a concentrator rather than a desorber and relies on incineration with catalytic oxidation to dispose of styrene captured in the adsorber (the Polyad Concentrator System). Both systems were described in Section 2.3 of this report. Weatherly Inc. certifies that either system will meet a guarantee of 95% styrene removal and a maximum outlet styrene concentration of 5 ppm. At the Eljer facility, installation of either Polyad system would require the addition of ducting to the present roof-vent system so that spray booth emissions would be directed to the Polyad system. However, these price quotes did not include stacks, manifolding, foundations, buildings, or weather protection.

Both systems were quoted on the same design basis with a nine-year depreciation period. Table 13 lists the design assumptions and price quote for each system and Table 14 provides an equipment list for each system. The air capacity of 200,000 scfm was based on the necessity of accommodating the output from all of the 14 available spray booths operating near their rated capacity of 14,500 acfm. An average inlet emissions level of 110 ppm of styrene was assumed and the temperature of the air entering the Polyad unit was assumed to be 30°C (86°F).

Table 13. Design Assumptions and Price Quotes for the Polyad Concentrator System and the Polyad Recovery System for the Eljer Facility

DESIGN ASSUMPTIONS

Air Capacity	200,000	scfm
Inlet Temperature	86	°F
Inlet Styrene Concentration	110	ppm
Outlet Styrene Concentration	5	ppm Maximum
Total System Efficiency	>95	%
Operation	1	shift/day
Hours of Operation per Year	2000	hours
Period of Depreciation	9	years
Cost of Electrical Power	0.04	\$/kWh
Cost of Natural Gas	1.50	\$/MM Btu
Cost of Steam	2.00	\$/1000 lb
Cost of Bonopore Adsorbent	21.00	\$/lb

POLYAD RECOVERY SYSTEM*

Installed Cost	5,000,000.00	\$
Total Cost	1828.00	\$/ton of styrene removed (over 9 year life)
	29.32	\$/scfm (over 9 year life)
Utility Consumption		
Electrical Power	690	kWh
Steam	595	lb/hour
Cooling Water	82	gal/min
Bonopore Adsorbent	4800	lb/year

POLYAD CONCENTRATOR SYSTEM*

Installed Cost	2,340,000.00	\$
Total Cost	886.00	\$/ton of styrene removed (over 9 year life)
	14.21	\$/scfm (over 9 year life)
Utility Consumption		
Electrical Power	690	kWh
Natural Gas	0.05	10 ⁶ Btu/hour
Instrument Air	80	psig
Bonopore Adsorbent	1200	lb/year

* Delivery 8 months after receipt of order. Not included in the system price or equipment list is a stack, manifolding, foundations, buildings, or weather protection.

Table 14. Equipment List and Dimensions for Large Components for Polyad Systems Suitable for Installation at the Eljer Facility

POLYAD RECOVERY SYSTEM*

<u>Quantity</u>	<u>Equipment Description</u>	<u>Foot Print</u>
2	Filter Unit	
2	Fluid Bed Adsorber Unit	16 ft x 40 ft
2	Cyclone	
2	Main Fan	
2	Moving Bed Desorber Unit	14 ft x 14 ft
2	Transport Fan	
2	Condenser Unit Fan	
2	Styrene Condenser Unit	
1	Styrene Recovery Tank	
2	Water Chiller	
2	Static Separator	

Necessary pipes and valves between units
 Electrical and Instrumental Equipment
 Bonopore for Initial Filling

POLYAD CONCENTRATOR SYSTEM*

<u>Quantity</u>	<u>Equipment Description</u>	<u>Foot Print</u>
2	Filter Unit	
2	Fluid Bed Adsorber Unit	16 ft x 40 ft
2	Cyclone	
2	Main Fan	
2	Fluid Bed Desorber Unit	
2	Desorber Unit	8 ft x 8.3 ft
2	Catalytic Oxidizer Unit	25 ft x 14 ft

Necessary pipes and valves between units
 Electrical and Instrumental Equipment
 Bonopore for Initial Filling

* Not included in the system price or equipment list is a stack, manifolding, foundations, buildings, or weather protection.

The Polyad Recovery System is identical in function to the Polyad mobile unit tested at Eljer Plumbingware. In order to recover styrene monomer, hot styrene-laden air from the moving bed desorber is passed through a solvent recovery unit where styrene is condensed and directed to a solvent recovery tank. Recovered solvent can be disposed of or reused. No attempt was made to estimate how cost savings from solvent reuse affect overall system cost because it may not be possible to use the recovered styrene monomer without distillation. In their quote for the PRS, Weatherly, Inc. noted that styrene has a tendency to discolor during recovery and in most cases requires distillation before it can be reused. This system was priced at \$5,000,000.00 (installed). Depreciated over a nine year lifetime, total cost (installation plus operation) is \$29.32/scfm or \$1828/ton of styrene removed.

It is possible to estimate the magnitude of savings that would be realized from the recovery of styrene over a nine-year lifetime for the Polyad Recovery System. In April of 1993, Mr. Rollie Nagel at Eljer Plumbingware reported that Eljer's current cost for styrene was \$0.68/lb, not including shipping or handling costs. At an average inlet concentration of 110 ppm, system flow rate of 200,000 scfm, and 2000 hour work year, in a period of 9 years, approximately 3048 tons of styrene would be recovered, assuming 95% recovery. Presuming that 75% of this styrene could be reused, without escalating the cost of styrene, a savings of approximately \$3,109,000 would be realized. If the cost of styrene escalated at 2.5% per year, the savings would be approximately \$3,437,000 over nine years. It should be noted that this estimate of savings does not include capital or operating costs of redistilling styrene (if needed), costs associated with disposing of spoiled or unusable recovered styrene, or manhour savings realized from the handling and storage of less fresh styrene monomer. What this simple analysis does indicate, however, is that solvent recovery may be cost effective.

The Polyad Concentrator System uses the same type of fluidized bed adsorber as was tested in the Polyad FB pilot unit. However, rather than cooling hot air from the desorber to condense styrene as was done in the pilot unit, hot styrene-laden air from the desorber (where styrene emissions are concentrated by a factor of 11.8) is sent to a catalytic oxidizer to be burned. Flow to the catalytic oxidizer is 17,000 acfm and because the styrene has been concentrated, combustion is self supporting within the oxidizer. Natural gas is required to start ignition and maintain a pilot light. This system was

priced at \$2,340,000.00 (installed). Depreciated over a nine year lifetime, total cost (installation plus operation) is \$14.21/scfm or \$886/ton of styrene removed.

Weatherly, Inc. also provided additional cost information for both types of Polyad systems. This cost information is shown in Figures 21 and 22. Figure 21 shows total cost (for a nine year operating life) in \$/ton of styrene removed as a function of styrene concentration at the inlet for two inlet flow rates: 20,000 and 60,000 scfm. Figure 22 also shows total system cost (for a nine year operating life) but in terms of \$/scfm as a function of the same inlet styrene concentrations for the same two inlet flow rates. On both figures total cost information for the proposed 200,000 scfm Eljer Polyad system is shown at an inlet styrene concentration of 110 ppm.

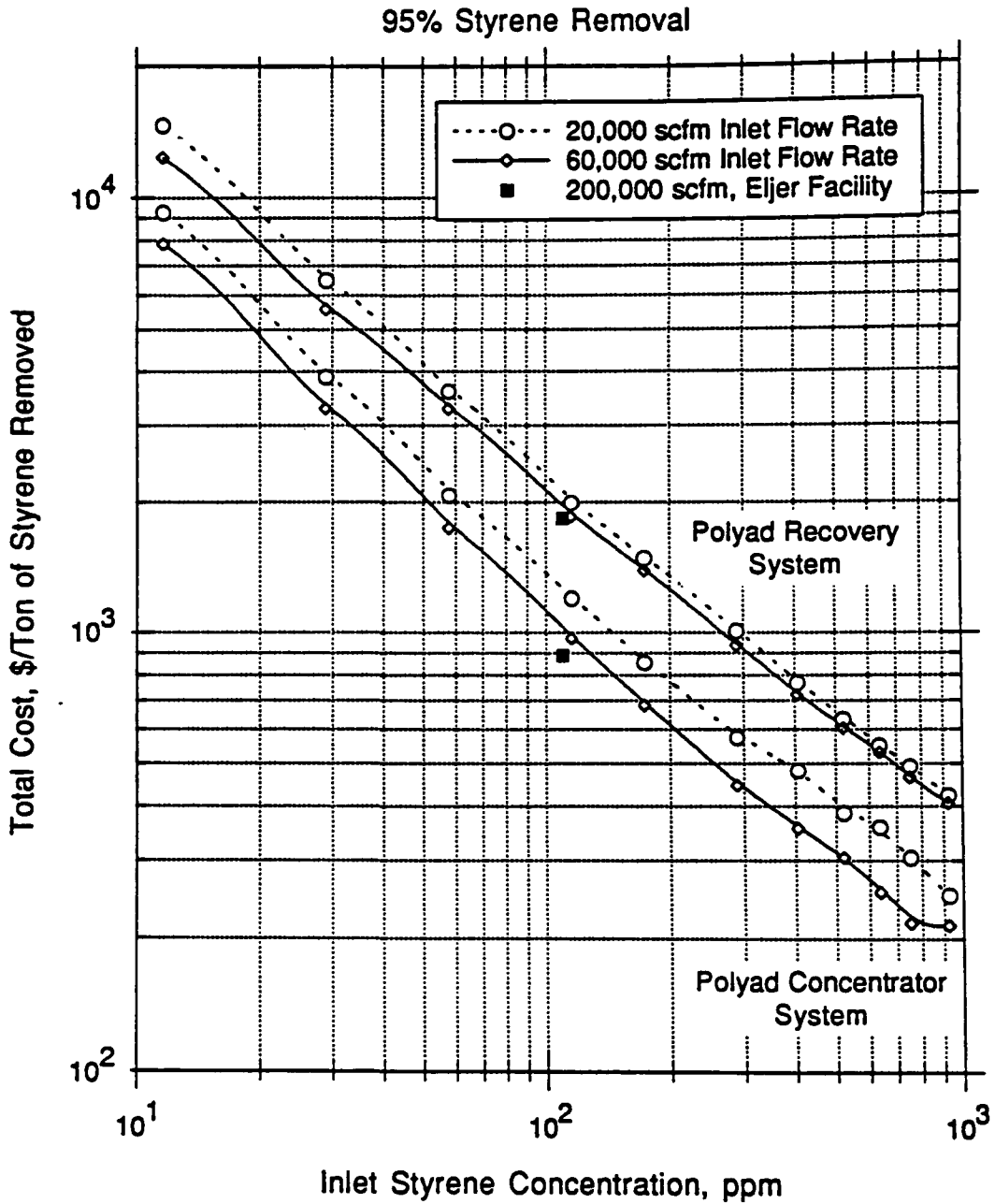


Figure 21. Total system cost as \$/ton of styrene removed for a nine year lifetime for various inlet concentrations of styrene. Data for 20,000 and 60,000 scfm inlet flow rates are shown along with values for the 200,000 scfm system proposed for Eljer Plumbingware

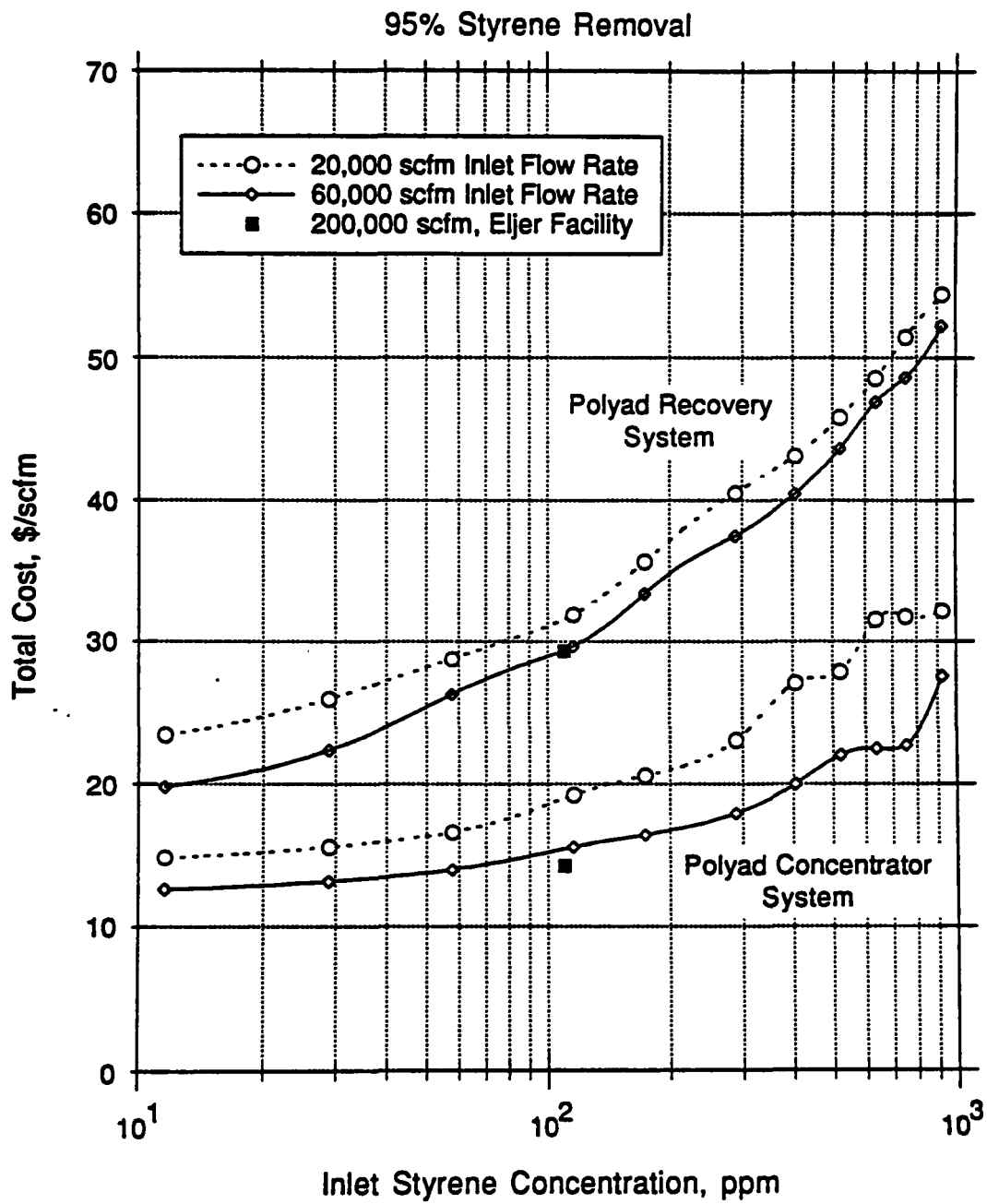


Figure 22. Total system cost as \$/scfm of inlet flow rate for a nine year lifetime for various inlet concentrations of styrene. Data for 20,000 and 60,000 scfm inlet flow rates are shown along with values for the 200,000 scfm system proposed for Eljer Plumbingware

SECTION 5

SUMMARY AND CONCLUSIONS

The purpose of this study was to evaluate the Polyad and Chemtact processes for controlling styrene emissions at a representative fiberglass shower stall and bath tub manufacturing plant. Because the Chemtact unit could not be made available within the time frame allotted for this work, only the Polyad process was evaluated. The Polyad process was evaluated with the aid of a small, transportable Polyad FB (fluidized bed) unit supplied by Weatherly, Inc., who is responsible for domestic marketing and sales of the Polyad process. The evaluation was carried out from November 3 - 5, 1992 at the Eljer Plumbingware facility located in Wilson, NC.

The Polyad process uses successive beds of a proprietary regenerable adsorbent (Bonopore®) that are fluidized by incoming solvent-laden air. Clean air is exhausted to the atmosphere from the last bed through a cyclone (to recover bed material). Adsorbent is continually removed from the fluidized beds, heated to evolve adsorbed solvent, and returned to the fluidized beds. Solvent is evolved from the bed material in a vertical moving bed desorber and recovered in a separate water-cooled condenser..

Testing of the Polyad FB pilot unit was complicated by the fact that just before this evaluation the Polyad FB unit was operated at a chemical plant to remove naphthalene from a contaminated air stream. Unfortunately, at the conclusion of that test, the unit was not cleaned and residual naphthalene and naphthalene-related compounds were not desorbed from the Bonopore adsorbent in the unit.

Nevertheless, the Polyad FB device demonstrated that the Polyad process could achieve styrene removal efficiencies of 99%. After the first day of testing, when molds were being sprayed the unit operated at a styrene removal efficiency of 94% or greater. During the last day of testing, when most of the naphthalene from the last series of tests had been evolved, the Polyad FB unit achieved an average styrene removal efficiency of 95.4% (96.6% while molds were being sprayed).

The possibility exists that greater styrene removal efficiencies could have been reached. An engineer at Weatherly, Inc. indicated that the lowest available Bonopore mass flow rate for the Polyad

styrene monomer has a relatively high boiling point (146°C) and a longer residence time in the adsorption unit and the desorption unit (lower flow rate) would have resulted in greater solvent recovery and higher overall efficiency.

In addition to the evaluation of the Polyad process, it was possible to quantify styrene emissions in the spray booth exhaust to which the Polyad FB device was connected and from the exhausts of two other spray booths at the Eljer Facility. 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 85 to 150 ppm.

APPENDIX A
NIOSH METHOD 1501

HYDROCARBONS, AROMATIC

FORMULA: Table 1

METHOD: 1501

M.W.: Table 1

ISSUED: 2/15/84

OSHA, NIOSH, ACGIH: Table 2

PROPERTIES: Table 1

COMPOUNDS:	benzene	cumene	α -methylstyrene	styrene	vinyltoluene
(Synonyms in Table 1)	p-tert-butyltoluene	ethylbenzene	naphthalene	toluene	xylylene

SAMPLING

MEASUREMENT

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal,
100 mg/50 mg)

!TECHNIQUE: GAS CHROMATOGRAPHY, FID
!
!ANALYTES: hydrocarbons listed above

FLOW RATE, VOLUME: Table 3

!DESORPTION: 1 mL CS₂; stand 30 min

SHIPMENT: no special precautions

!INJECTION VOLUME: 5 μ L

SAMPLE STABILITY: not determined

!TEMPERATURE-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: N₂ or He, 25 mL/min

!COLUMN: glass, 3.0 m x 2 mm, 10% OV-275 on
100/120 mesh Chromosorb W-AW
or equivalent

ACCURACY

RANGE STUDIED,
BIAS and OVERALL PRECISION (s_p): Table 3

!CALIBRATION: analytes in CS₂

!RANGE AND PRECISION (s_p): Table 4

!ESTIMATED LOD: 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 (C₁₀). 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, toluene and xylylene [2]; S311, benzene [4]; S22, p-tert-butyltoluene [3]; S23, cumene [3]; S29, ethylbenzene [3]; S26, α -methylstyrene [3]; S292, naphthalene [4]; S30, styrene [3]; S343, toluene [4]; S25, vinyltoluene [3]; S318, xylylene [4].

REAGENTS:

1. Eluent: Carbon disulfide*, chromatographic quality containing (optional) suitable internal standard.
2. Analytes, reagent grade*
3. Nitrogen or helium, purified
4. Hydrogen, prepurified.
5. Air, filtered.
6. Naphthalene calibration stock solution, 0.40 g/mL in CS₂.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg, back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling 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. Pipet, 1-mL, and pipet bulb.
6. Syringes, 5-, 10-, 25- and 100- μ L.
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.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min (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. Add 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).

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
 - a. Remove and discard back sorbent section of a media blank sampler.
 - b. Inject a known amount of analyte (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.

MEASUREMENT:

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

Substance ^a	Approximate Retention Time (min), at Indicated Column Temperature			
	50 °C	100 °C	150 °C	Programmed ^b
benzene	2.5			2.5
toluene	4.3	1.1		4.2
xylene (<i>para</i>)	7.0	1.4		5.2
ethylbenzene	7.0	1.4		5.5
xylene (<i>meta</i>)	7.2	1.5		5.6
cumene	8.3	1.6		6.0
xylene (<i>ortho</i>)	10	1.9		6.5
styrene	16	2.6		7.6
<i>o</i> -methylstyrene		3.2	1.0	8.1
vinyltoluene (<i>meta</i>)		3.8	1.2	8.5
naphthalene		25	4.3	12

^aData not available for *p-tert*-butyltoluene and *p*-vinyltoluene.

^bTemperature 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_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.

NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.

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

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

EVALUATION OF METHOD:


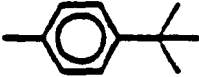
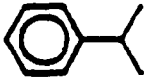
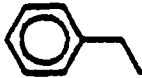
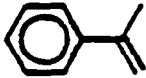

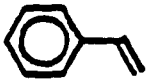
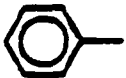
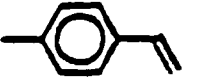

Precisions and biases listed in Table 3 were determined by analyzing generated atmospheres containing one-half, one, and two times the OSHA standard. Generated concentrations were independently verified. Breakthrough capacities were determined in dry air. Storage stability was not assessed. Measurement 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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- [5] R. D. Dreisbach. "Physical Properties of Chemical Compounds"; Advances in Chemistry Series, No. 15; American Chemical Society, Washington (1955).
- [6] Code of Federal Regulations; Title 29 (Labor), Parts 1900 to 1910; U.S. Government Printing Office, Washington (1980); 29 CFR 1910.1000.
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- [12] Documentation of the NIOSH Validation Tests, S22, S23, S25, S26, S29, S30, S292, S311, S318, S343, U.S. Department of Health, Education, and Welfare; Publ. (NIOSH) 77-185 (1977).

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

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

Name/Synonyms	Structure	Empirical Formula	Molec- ular Weight	Boiling Point (°C)	Vapor Pressure @ 25 °C		Density @ 20 °C (g/mL)
					(mm Hg)	(kPa)	
benzene CAS #71-43-2		C ₆ H ₆	78.11	80.1	95.2	12.7	0.879
p-tert-butyltoluene CAS #98-51-1 1-tert-butyl-4-methylbenzene		C ₁₁ H ₁₆	148.25	192.8	0.7	0.09	0.861
cumene CAS #98-82-8 isopropylbenzene		C ₉ H ₁₂	120.20	152.4	4.7	0.62	0.862
ethylbenzene CAS #100-41-4		C ₈ H ₁₀	106.17	136.2	9.6	1.28	0.867
α-methylstyrene CAS #98-83-9 isopropenylbenzene (1-methylethenyl)-benzene		C ₉ H ₁₀	118.18	165.4	2.5	0.33	0.911
naphthalene CAS #91-20-3		C ₁₀ H ₈	128.18	80.2 ^a	0.2	0.03	1.025
styrene CAS #100-42-5 vinylbenzene		C ₈ H ₈	104.15	145.2	6.1	0.81	0.906
toluene CAS #108-88-3 methylbenzene		C ₇ H ₈	92.14	110.6	28.4	3.79	0.867
vinyltoluene ^b CAS #25013-15-4 methylstyrene methylvinylbenzene	 (p-vinyltoluene)	C ₉ H ₁₀	118.18	167.7	1.6	0.22	0.898
			(<u>meta</u>)	171.6	1.9	0.26	0.911
			(<u>para</u>)	172.8	1.8	0.24	0.911
xylene ^c CAS #1330-20-7 dimethylbenzene	 (p-xylene)	C ₈ H ₁₀	106.17	144.4	6.7	0.89	0.880
			(<u>ortho</u>)	139.1	8.4	1.12	0.864
			(<u>para</u>)	138.4	8.8	1.18	0.861

^aMelting point.^bCommercial mixture of meta and para isomers.^cMixture of isomers.

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

Substance	OSHA			NIOSH		ACGIH		mg/m ³ per ppm
	TWA	C	Peak	TWA	C	TLV	STEL	
benzene	10	25	50 ^a	1		10 ^{**}	25 ^{**}	3.19
p-tert-butyltoluene	10					10	20	6.06
cumene	50 (skin)					50	75 (skin)	4.91
ethylbenzene	100					100	125	4.34
α-methylstyrene		100				50	100	4.83
naphthalene	10					10	15	5.24
styrene	100	200	600 ^b	50	100	50	100	4.26
toluene	200	300	500 ^a	100	200*	100	150 (skin)	3.77
vinyltoluene	100					50	100	4.83
xylene	100			100	200*	100	150	4.34

^aMaximum duration 10 min in 8 hr.^{**}ACGIH: suspect carcinogen [10].^bMaximum duration 5 min in any 3 hr.

* 10-min sample.

Table 3. Sampling flowrate^a, volume, capacity, range, overall bias and precision [3,4,12].

Substance	Sampling			Breakthrough		Range	Overall	
	Flowrate (L/min)	Volume (L)		Volume @ Concentration		at VOL-NOM	Bias (%)	Precision (s _p)
		VOL-NOM	VOL-MAX ^b	(L)	(mg/m ³)	(mg/m ³)		
benzene	≤0.20	2 ^c	30	>45	149	42- 165	0.8	0.059
p-tert-butyltoluene	≤0.20	10	29	44	112	29- 119	-10.4	0.071 ^d
cumene	≤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 ^d
α-methylstyrene	≤0.20	3 ^f	30	>45	940	236- 943	-10.8	0.061 ^d
naphthalene ^e	≤1.0	200	200	>240	81	19- 83	-0.5	0.055
styrene	≤1.0	5 ^g	14	21	1710	426-1710	-10.7	0.058 ^d
toluene	≤0.20	2 ^c	8	12	2294	548-2190	3.8	0.052
vinyltoluene	≤0.20	10	24	36	952	256- 970	-9.5	0.061 ^d
xylene	≤0.20	12	23	35	870	218- 870	-2.1	0.060

^aMinimum recommended flow is 0.01 L/min.^bApproximately two-thirds the breakthrough volume, except for naphthalene.^c10-min sample.^dCorrected value, calculated from data in Reference 12.^eNaphthalene shows poor desorption efficiency at low loading; 100-L minimum volume is recommended.^f15-min sample.^g95-min sample.

Table 4. Measurement range, precision and conditions^a [3,4,12].

Substance	Desorption Volume (mL)	Measurement		Carrier Flow (mL/min)	Column Parameters ^b		
		Range (mg)	Precision (s _r)		t (°C)	Length (m)	Packing ^c
benzene	1.0	0.09- 0.35	0.036	50	115	0.9	A
<i>p</i> - <i>tert</i> -butyltoluene	0.5	0.27- 1.09	0.021 ^d	50	115	3.0	B
cumene	0.5	0.86- 3.46	0.010	50	99	3.0	B
ethylbenzene	0.5	2.17- 8.67	0.010	50	85	3.0	B
<i>o</i> -methylstyrene	0.5	0.69- 3.57	0.011	50	115	3.0	B
naphthalene	1.0	4.96-19.7	0.019	30	125	3.0	C
styrene	0.5	2.17- 8.49	0.013 ^d	50	109	3.0	B
toluene	1.0	1.13- 4.51	0.011	50	155	0.9	D
vinyltoluene	0.5	2.41- 9.64	0.008	50	120	3.0	B
xylene	1.0	2.60-10.4	0.010	50	180	0.9	D

^aInjection volume, 5.0 μ L; 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 AW-DMCS;

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

^dCorrected value, calculated from data in [12].

APPENDIX B
QUALITY CONTROL EVALUATION REPORT

SUMMARY

A Quality Assurance Project Plan (QAPP) was written and approved for this project before testing began. No field audits were planned or performed. However, as stated in the QAPP, certified calibration gases (28, 55, and 192 ppm of styrene in nitrogen and zero air with less than 0.1 ppm THC content) served as field performance audit samples for NIOSH Method 1501 and THC sampling. Also, 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 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.

Overall, data quality indicator (DQI) goals were achieved. However, some data were lost due to an equipment malfunction and because of that malfunction much less data were obtained from the NIOSH Method 1501 samples than was planned. Since these measurements were duplicated by the THC analyzer measurements, overall objectives of the project were not compromised.

SIGNIFICANT QA/QC PROBLEMS

One significant QA/QC problem was encountered. Styrene concentrations determined from charcoal tube samples taken at the inlet and outlet of the Polyad FB mobile pilot unit were not reliable because the sample pumps used to draw air samples through the charcoal tubes were unable to maintain correct flow at inlet pressures negative with respect to ambient. This problem was not discovered until after all field sampling was completed primarily because the bubble flow meter used to calibrate the sample pumps could not be operated at inlet pressures negative with respect to ambient. After this problem was discovered, numerous attempts were made to simulate the sampling conditions

under which the samples were taken so that sample flow rates could be corrected. However, these attempts were not successful. No other corrective actions were required or taken during the collection of samples and data or during subsequent analysis of samples collected during testing.

DATA QUALITY

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

- Precision is expressed as percent coefficient of variation:

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

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

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

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

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

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

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

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

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-1 shows the DQI goals that were estimated for critical measurements in the QAPP. Tables B-2 and B-3 show DQI values for measurements carried out with charcoal tubes (NIOSH Method 1501). Table B-4 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

Triplicate charcoal tube samples taken on October 13, 1992 and on November 6, 1992 provided a total of 12 samples from which precision for this method could be estimated. Details and results of these measurements are shown in Tables 6 and 7 of this report. Three series of runs were made. Six separate runs were made at the same time at gel coat booth #2 on October 13, 1992 and two sets of triplicate runs were made on November 6, 1992 after sampling was completed at gel coat booth #2 (one set at first lay-up booth #5 and one set at second lay-up booth #7). An outlier was identified in the first set of 6 runs made on October 13, 1992 and was not included in results reported in Table B-2. Precision for the three distinct sets of runs averaged 6.6%, greater than the 5.8% expected for NIOSH Method 1501. However, if the third sample taken at second lay-up booth #7 on November 6, 1992 is excluded, the average precision drops to approximately 4%.

Table B-1. 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	1. Inlet and Outlet of control device, 2. Calibration gas samples.	5.8 ¹	-10.7 ¹	85
Total Hydrocarbon Analyzer with FID. ²	Hydrocarbon compounds in air.	1. Inlet and Outlet of control device, 2. Calibration gas samples.	± 10 ³	± 5 ³	85

¹ Precision and bias for sampling with charcoal-filled tube.

² J.U.M. Model VE-7 THC Analyzer.

³ Estimated values. Precision and bias will be determined for each instrument

**Table B-2. Data Quality Indicator Values for NIOSH Method 1501
Measurements Made at Eljer Plumbingware**

Method and Reference	Measurement Parameter	Experimental Condition	Precision (Rel. Std. Dev., %)*	Accuracy (% Bias)	Completeness (%)
NIOSH 1501	Styrene Content	1 Gel Coat Booth #2 Exhaust, 10/13/92	4.3	N/A	83.3
		2. First Lay-Up Booth #5 Exhaust, 11/6/92	3.6	N/A	100
		3. Second Lay-Up Booth #7 Exhaust, 11/6/92	11.9	N/A	100

* Precision for sampling with charcoal-filled tube. Average of three conditions = 6.6%

Table B-3. Data Quality Indicator Values for NIOSH Method 1501 Charcoal Sample Tubes Spiked with Known Concentrations of Styrene

Known Styrene Content (µg/ml)	Recovered Styrene Content (µg/ml)	Bias* (%)	Precision (%)
90.6	73.7	-18.65	-
181.2	181.1	-0.06	-
181.2	231.0	27.48	-
453.0	338.7	-25.23	-
1812	1750	-3.42	
1812	1938	6.95	
1812	1643	-9.33	8.4
3624	3831	5.71	
3624	3590	-0.94	
3624	3764	3.86	3.3
7248	7103	-2.00	-
	Average	-1.42	5.9

* Expressed as Relative Percent Difference

**Table B-4. Data Quality Indicator Values for THC Analyzer
Measurements Made at Eljer Plumbingware**

INLET THC ANALYZER

Span Gas/% Bias	25 ppm Span Gas (Measured Value)	Bias %	49 ppm Span Gas (Measured Value)	Bias %	171 ppm Span Gas (Measured Value)	Bias %
	25.0	0.0	53.1	8.0	172.5	0.5
	27.0	8.0	51.1	4.0	171.7	0.0
	25.0	0.0	50.8	3.4	164.8	-4.0
	27.6	10.4			170.0	-1.0
	27.8	11.2				
	24.1	-3.6				
Precision (% CV)	6.0		2.4		2.0	
Average % Bias		4.3		5.1		-1.1

OUTLET THC ANALYZER

Span Gas/% Bias	25 ppm Span Gas (Measured Value)	Bias %	49 ppm Span Gas (Measured Value)	Bias %	171 ppm Span Gas (Measured Value)	Bias %
	25.0	0.0	53.1	8.0	168.2	-2.0
	26.0	4.0	48.1	-2.2	175.1	2.0
	25.0	0.0	51.1	4.0	159.7	-7.0
	24.3	-2.8			169.1	-1.5
	26.0	4.0			171.7	0.0
	26.2	4.8				
Precision (% CV)	3.0		5.0		3.8	
Average % Bias		1.7		3.3		-1.7

Table B-3 shows the results of measurements made with charcoal tubes spiked with a known amount of styrene monomer. These data were fit with a linear regression ($R^2 = 0.9969$) to quantify the results of GC-FID measurements made on styrene desorbed from the charcoal tube samples taken during testing. Two concentrations were spiked in triplicate (1812 and 3624 $\mu\text{g/ml}$). The precision measured for these two sets averaged 5.9%.

For THC analyzer measurements, precision was determined from repeated measurements of the three span gases. Averaged precision values for the inlet and outlet THC analyzers reported in Table B-3 (3.5% for the inlet THC and 3.9% for the outlet THC) are approximately one-third of that originally estimated in Table B-1.

Bias

Bias could not be determined from charcoal tube samples obtained during testing at Eljer Plumbingware because of the problems in sampling reported above. However charcoal tubes spiked with known concentrations of styrene were prepared and analyzed at SRI. The results of this analysis are reported in Table B-3. For some of the lower concentrations listed, several bias values (as relative percent difference) in this table are rather high. However, on the average, bias was low (-1.4%).

For THC analyzer measurements, bias was determined for each measurement made of the three span gases and are reported in Table B-3. Average bias values for the inlet THC ran from -1.1% (192 ppm styrene) to 5.1% (55 ppm styrene). Average bias values for the outlet THC ran from -1.7% (192 ppm styrene) to 3.3% (55 ppm styrene). Overall, bias values were within the $\pm 5\%$ estimated in Table B-1.

Completeness

For the NIOSH Method 1501 samples taken at the inlet and outlet of the Polyad FB device, completeness was 0% because styrene concentration could not be determined from any of the samples. From the NIOSH Method 1501 samples taken before and after testing the Polyad FB device completeness was 91.7%.

For THC analyzer measurements, completeness was much higher. Some data was lost during FID flame-outs and other data was lost during a power failure on the last day of testing. Out of

approximately 12.3 hours of data (at one data point per second) less than 5 minutes worth of data were lost due to FID flame-outs (completeness of 99.3%). Including in a power failure of 15 minutes when no data were obtained, completeness was 97.3%.

Representativeness

The design of the portable Polyad FB device 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 the high flow velocity into the Polyad FB unit (4-6 m/sec) assured that the sample extracted from the gel coat booth #2 exhaust was representative. Following the sample methodology recommended in NIOSH Method 1501 and EPA Method 18 (Section 7.4) 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. However, because the NIOSH 1501 samples taken coincident with the THC sampling periods were unusable, no such comparison can be made. Nonetheless, since measured precision and accuracy of the THC data were both well within our DQI objectives, we feel confident that the overall objectives of the project were not compromised.

APPENDIX C
TOTAL HYDROCARBON ANALYZER DAILY RESULTS

Table C-1. THC Analyzer Results from November 3, 1992, First Period of Spraying

November 3, 1992		Elapsed Time (seconds)	INLET THC (ppm)			OUTLET THC (ppm)		
Start Time	End Time		Average	Population Std. Dev.	95% Conf. Interval	Average	Population Std. Dev.	95% Conf. Interval
9:04	9:08	262	165.7	81.8	9.9	21.52	0.14	0.02
9:08	9:08	8	61.1	0.8	0.5	21.37	0.04	0.04
9:09	9:09	10	60.5	1.2	0.7	21.31	0.06	0.04
9:09	9:09	6	63.7	0.6	0.4	21.24	0.01	0.01
9:09	9:09	3	63.3	0.5	0.6	21.24	0.04	0.04
9:09	9:12	218	41.0	5.7	0.8	21.09	0.13	0.02
9:12	9:16	217	176.9	58.1	7.7	20.64	0.11	0.02
9:16	9:16	23	55.9	3.7	1.5	20.50	0.04	0.02
9:16	9:22	306	195.7	59.4	6.6	20.39	0.08	0.01
9:22	9:25	182	45.8	5.6	0.8	20.20	0.10	0.02
9:25	9:30	304	171.9	55.0	6.2	19.87	0.14	0.02
9:30	9:32	145	45.5	5.4	0.9	19.61	0.05	0.01
9:32	9:33	31	99.9	22.3	7.9	19.56	0.05	0.02
9:33	9:33	30	53.4	4.0	1.4	19.59	0.05	0.02
9:33	9:39	359	202.3	80.1	8.3	19.53	0.08	0.01
9:39	9:40	42	54.2	4.8	1.4	19.38	0.06	0.02
9:40	9:41	100	49.1	4.3	0.8	19.21	0.05	0.01
9:41	9:47	302	190.4	87.6	9.8	18.94	0.17	0.02
9:47	9:48	64	52.5	5.2	1.3	18.57	0.05	0.02
9:48	9:54	409	131.0	68.3	6.6	18.14	0.23	0.03
9:54	9:55	9	64.9	1.3	0.9	17.68	0.03	0.02
9:55	9:55	6	59.1	1.7	1.3	17.67	0.03	0.02
9:55	9:55	3	63.6	0.2	0.2	17.65	0.02	0.02
9:55	9:55	6	59.6	1.4	1.2	17.65	0.04	0.03
9:55	9:55	3	64.5	1.2	1.3	17.71	0.00	0.01
9:55	9:57	134	41.6	9.1	1.5	17.46	0.15	0.03
9:57	10:01	246	183.3	59.7	7.4	16.71	0.23	0.03
Emissions > 63 PPM		2460	173.7			19.40		
Emissions < 63 PPM		968	46.1			19.66		
All Emissions		3428	137.7			19.47		

71.8 % of time spent spraying, 9:04 - 10:01 AM

Table C-2. THC Analyzer Results from November 3, 1992, Second Period of Spraying

November 3, 1992		Elapsed Time (seconds)	INLET THC (ppm)			OUTLET THC (ppm)		
Start Time	End Time		Average	Population Std. Dev.	95% Conf. Interval	Average	Population Std. Dev.	95% Conf. Interval
10:01	10:18	1014	34.9	9.4	0.5	14.28	1.07	0.06
10:18	10:23	287	205.3	55.7	6.4	12.04	0.22	0.03
10:23	10:23	5	60.4	1.3	1.2	11.66	0.03	0.03
10:23	10:25	150	33.2	7.7	1.3	11.35	0.16	0.03
10:26	10:27	78	28.3	6.9	1.5	10.96	0.07	0.02
10:27	10:27	5	70.3	3.5	3.0	10.87	0.02	0.02
10:27	10:28	70	29.8	8.9	2.1	10.69	0.06	0.02
10:28	10:32	227	218.9	74.2	9.7	10.32	0.14	0.02
10:32	10:32	10	60.3	1.9	1.2	10.06	0.02	0.01
10:32	10:36	226	206.6	73.0	9.5	9.74	0.19	0.03
10:36	10:37	81	49.7	4.2	0.9	9.32	0.08	0.02
10:37	10:38	56	131.0	60.9	15.9	9.18	0.04	0.01
10:38	10:38	4	58.7	2.1	2.1	9.17	0.02	0.02
10:38	10:38	5	58.6	2.0	1.7	9.14	0.03	0.03
10:38	10:38	13	54.5	4.0	2.1	9.10	0.03	0.02
10:38	10:42	234	224.3	88.2	11.3	8.81	0.18	0.03
10:42	10:49	375	37.2	8.0	0.8	8.07	0.23	0.03
10:49	10:49	42	127.6	52.9	16.0	7.71	0.04	0.01
10:49	10:50	25	52.8	4.8	1.9	7.69	0.04	0.02
10:50	10:56	393	205.0	77.8	7.7	7.39	0.19	0.02
10:56	11:00	195	36.3	5.7	0.8	6.93	0.08	0.01
11:00	11:07	433	205.1	70.6	6.6	6.63	0.12	0.01
11:07	11:07	4	61.2	0.6	0.6	6.51	0.02	0.02
11:07	11:07	3	63.9	1.1	1.3	6.47	0.01	0.02
11:07	11:08	67	44.7	5.6	1.3	6.44	0.04	0.01
11:08	11:14	375	214.1	78.1	7.9	6.54	0.15	0.02
11:14	11:15	32	51.5	4.9	1.7	6.79	0.03	0.01
11:15	11:15	5	67.4	2.2	2.0	6.80	0.03	0.03
11:15	11:18	186	40.1	4.0	0.5	6.90	0.08	0.01
11:18	11:21	208	216.5	79.6	10.8	7.02	0.06	0.01
11:21	11:22	5	67.4	2.2	2.0	6.89	0.01	0.01
11:22	11:27	337	39.3	8.8	1.0	6.92	0.11	0.01
11:27	11:35	449	202.9	74.2	6.9	6.54	0.14	0.01
11:35	11:35	3	61.1	0.4	0.4	6.29	0.03	0.04
11:35	11:35	6	67.0	2.9	2.3	6.27	0.01	0.01
11:35	11:38	206	34.3	4.5	0.6	6.24	0.04	0.01
11:38	11:42	232	220.5	66.1	8.5	6.10	0.05	0.01
11:42	11:47	295	42.0	6.7	0.8	6.02	0.06	0.01
11:47	11:48	37	199.5	69.6	22.4	6.06	0.03	0.01
Emissions > 63 PPM		3223	206.8			7.86		
Emissions < 63 PPM		2141	38.7			7.64		
All Emissions		5364	139.7			7.77		

60.1 % of time spent spraying, 10:01 - 11:48 AM

* Outlier, from period at beginning of spraying.

Table C-3. THC Analyzer Results from November 3, 1992, Third Period of Spraying

November 3, 1992		Elapsed Time (seconds)	INLET THC (ppm)			OUTLET THC (ppm)		
Start Time	End Time		Average	Population Std. Dev.	95% Conf. Interval	Average	Population Std. Dev.	95% Conf. Interval
12:54	12:55	26	281.2	11.0	4.2	*	*	*
12:55	12:59	263	28.5	2.6	0.4	4.92	0.04	0.01
12:59	13:04	273	186.6	88.2	10.5	4.82	0.05	0.01
13:04	13:04	3	61.9	0.6	0.7	4.69	0.02	0.03
13:04	13:05	45	75.2	5.5	1.6	4.70	0.03	0.01
13:05	13:08	231	28.1	6.8	0.9	4.67	0.04	0.00
13:08	13:09	54	121.8	41.2	11.0	4.63	0.04	0.01
13:09	13:10	9	57.3	5.5	3.6	*	*	*
13:10	13:16	411	160.1	80.3	7.8	4.79	0.04	0.00
13:16	13:19	151	28.3	7.0	1.1	4.77	0.03	0.01
13:19	13:23	262	177.5	55.4	6.7	4.73	0.04	0.01
13:23	13:26	192	31.0	6.2	0.9	4.67	0.03	0.00
13:26	13:29	174	192.3	65.6	9.7	4.67	0.04	0.01
13:29	13:33	220	39.4	6.5	0.9	4.69	0.04	0.00
13:33	13:37	218	181.0	67.9	9.0	4.71	0.04	0.00
13:37	13:37	3	61.0	1.2	1.3	4.75	0.03	0.03
13:37	13:40	184	48.4	4.9	0.7	4.77	0.06	0.01
13:40	13:44	265	190.5	80.0	9.7	4.91	0.04	0.00
13:44	13:48	207	42.4	5.5	0.7	4.93	0.04	0.01
13:48	13:53	336	179.0	77.1	8.2	4.95	0.04	0.01
13:53	13:55	126	38.5	4.6	0.8	5.09	0.03	0.01
13:55	14:01	342	164.6	78.4	8.3	5.08	0.04	0.00
14:01	14:02	78	41.5	8.0	1.8	5.05	0.04	0.01
14:02	14:07	286	195.7	68.4	8.0	4.52	1.69	0.20
**	14:07	729	27.4	10.4	0.7	5.16	0.04	0.00
Emissions > 63 PPM		2692	176.9			4.81		
Emissions < 63 PPM		1667	35.7			4.81		
All Emissions		4359	122.9			4.81		

- 61.8 % of time spent spraying, 12:54 - 2:21 PM
- * Data lost due to flame out of FID in outlet THC analyzer.
- ** Outlier, from period at end of spraying.

Table C-4. THC Analyzer Results from November 4, 1992, First Period of Spraying

November 4, 1992		Elapsed Time (seconds)	INLET THC (ppm)			OUTLET THC (ppm)		
Start Time	End Time		Average	Population Std. Dev.	95% Conf. Interval	Average	Population Std. Dev.	95% Conf. Interval
8:42	8:45	169	164.8	60.1	9.0	14.88	0.17	0.03
8:45	8:48	208	41.3	6.4	0.9	14.18	0.12	0.02
8:48	8:53	317	136.4	63.3	7.0	13.50	0.26	0.03
8:53	8:54	3	61.6	0.8	0.9	13.02	0.04	0.04
8:54	8:54	5	65.9	2.5	2.1	12.99	0.02	0.02
8:54	8:54	22	69.6	3.6	1.5	12.96	0.03	0.01
8:54	8:54	6	61.1	0.8	0.7	12.93	0.02	0.02
8:54	8:55	28	65.8	2.1	0.8	12.88	0.03	0.01
8:55	8:55	3	62.1	0.4	0.4	12.87	0.00	-
8:55	8:55	5	64.9	0.8	0.7	12.85	0.02	0.02
8:55	8:55	6	61.5	0.8	0.6	12.84	0.01	0.01
8:55	8:55	4	64.7	1.2	1.2	12.83	0.00	0.00
8:55	8:55	3	63.2	0.6	0.7	12.83	0.02	0.02
8:55	8:55	17	60.0	1.3	0.6	12.86	0.03	0.01
8:55	8:55	15	77.8	6.8	3.4	12.80	0.04	0.02
8:56	8:56	49	58.3	2.2	0.6	12.75	0.04	0.01
8:56	8:56	7	68.3	3.9	3.0	12.70	0.02	0.02
8:56	8:58	120	36.7	6.6	1.2	12.48	0.11	0.02
8:58	8:59	46	112.2	39.4	11.4	12.27	0.04	0.01
8:59	8:59	7	58.1	2.1	1.6	12.21	0.02	0.01
8:59	9:08	502	139.3	64.7	5.6	11.52	0.38	0.04
9:08	9:09	54	44.8	7.1	1.9	10.77	0.04	0.01
9:09	9:13	283	167.6	67.2	7.9	10.39	0.21	0.03
9:13	9:15	108	46.7	5.7	1.1	10.00	0.06	0.01
9:15	9:21	336	165.8	59.9	6.4	9.68	0.11	0.01
9:21	9:24	217	39.9	5.3	0.7	9.36	0.09	0.01
9:24	9:28	245	176.0	54.1	6.8	9.01	0.13	0.02
9:28	9:29	33	58.1	2.0	0.7	8.74	0.04	0.01
9:29	9:29	27	66.6	1.7	0.6	8.66	0.03	0.01
9:29	9:30	6	64.2	0.8	0.6	8.61	0.02	0.01
9:30	9:32	155	53.6	3.6	0.5	8.46	0.10	0.02
9:32	9:35	195	190.0	57.1	8.0	8.09	0.19	0.03
9:35	9:36	28	57.6	2.7	1.0	7.66	0.05	0.02
9:36	9:36	18	68.3	2.6	1.2	7.53	0.04	0.02
9:36	9:36	4	61.2	0.6	0.6	7.45	0.02	0.02
9:36	9:36	9	65.0	1.5	1.0	7.44	0.03	0.02
9:36	9:37	9	60.6	1.0	0.6	7.40	0.03	0.02
9:37	9:37	15	66.6	2.5	1.3	7.38	0.02	0.01
9:37	9:37	15	58.5	2.8	1.4	7.34	0.02	0.01
9:37	9:43	355	181.9	68.6	7.2	7.14	0.12	0.01
9:43	9:46	174	42.9	7.4	1.1	6.88	0.06	0.01
9:46	9:50	240	155.3	67.7	8.6	6.61	0.13	0.02
9:50	9:50	5	65.2	1.4	1.3	6.41	0.04	0.03
9:50	9:51	75	45.0	4.3	1.0	6.39	0.03	0.01
9:51	9:57	372	134.7	68.0	6.9	6.22	0.09	0.01
9:57	10:05	480	37.5	4.0	0.4	5.90	0.11	0.01
Emissions > 63 PPM		3229	152.6			9.69		
Emissions < 63 PPM		1291	45.6			10.07		
All Emissions		4520	122.0			9.80		

71.4 % of time spent spraying, 8:42 - 10:05 AM

• Outlier, from period at end of spraying.

Table C-5. THC Analyzer Results from November 4, 1992, Second Period of Spraying

November 4, 1992		Elapsed Time (seconds)	INLET THC (ppm)			OUTLET THC (ppm)		
Start Time	End Time		Average	Population Std. Dev.	95% Conf. Interval	Average	Population Std. Dev.	95% Conf. Interval
10:12	10:20	501	19.0	2.8	0.3	5.36	0.10	0.01
10:20	10:24	221	218.1	73.6	9.7	5.28	0.03	0.00
10:24	10:24	26	50.4	5.7	2.2	5.33	0.03	0.01
10:24	10:28	259	217.6	69.4	8.4	5.31	0.04	0.00
10:28	10:33	285	40.4	5.9	0.7	5.33	0.04	0.00
10:33	10:38	300	192.0	62.4	7.1	5.36	0.04	0.00
10:38	10:51	752	37.8	4.8	0.4	5.30	0.06	0.00
10:51	10:52	56	138.7	58.9	15.5	5.41	0.04	0.01
10:52	10:52	34	54.9	3.8	1.3	5.41	0.03	0.01
10:52	10:59	393	187.9	69.3	6.9	5.41	0.04	0.00
10:59	10:59	4	60.8	1.4	1.4	5.43	0.02	0.02
10:59	10:59	6	68.6	3.4	2.7	5.40	0.02	0.02
10:59	10:59	38	49.2	4.8	1.5	5.40	0.03	0.01
11:00	11:00	50	124.5	43.8	12.2	5.37	0.03	0.01
11:00	11:00	4	59.7	1.3	1.3	5.34	0.03	0.03
11:00	11:00	5	65.5	0.7	0.6	5.36	0.02	0.02
11:00	11:01	4	62.1	0.4	0.4	5.33	0.01	0.01
11:01	11:01	3	64.2	1.0	1.2	5.35	0.01	0.01
11:01	11:01	31	54.0	3.0	1.1	5.36	0.04	0.01
11:01	11:07	335	177.6	72.5	7.8	5.41	0.04	0.00
11:07	11:09	111	49.7	4.9	0.9	5.48	0.05	0.01
11:09	11:14	322	212.8	81.5	8.9	5.67	0.06	0.01
11:14	11:14	3	61.9	0.4	0.4	5.80	0.04	0.05
11:14	11:14	5	63.8	0.4	0.4	5.78	0.01	0.01
11:14	11:14	14	56.4	2.1	1.1	5.81	0.04	0.02
11:14	11:18	206	186.6	69.1	9.5	5.83	0.04	0.01
11:18	11:18	4	60.8	1.3	1.3	5.86	0.01	0.01
11:18	11:18	6	64.5	0.4	0.4	5.87	0.04	0.03
11:18	11:18	6	61.2	0.9	0.7	5.89	0.04	0.03
11:18	11:18	3	64.4	1.0	1.1	5.93	0.01	0.01
11:18	11:18	7	61.5	0.9	0.6	5.92	0.03	0.03
11:18	11:18	4	65.6	1.9	1.9	5.89	0.01	0.01
11:18	11:18	6	59.8	1.8	1.4	5.88	0.02	0.01
11:18	11:18	6	64.7	1.1	0.9	5.88	0.02	0.02
11:18	11:19	39	58.3	1.5	0.4	5.92	0.04	0.01
11:19	11:19	13	72.6	6.5	3.6	5.95	0.04	0.02
11:19	11:19	5	57.6	2.9	2.5	5.94	0.03	0.02
11:19	11:27	437	186.8	72.6	6.8	6.03	0.08	0.01
11:27	11:27	16	59.9	1.4	0.7	6.06	0.03	0.01
11:27	11:31	252	206.6	72.8	9.0	6.09	0.04	0.00
11:31	11:31	3	60.5	0.5	0.6	6.09	0.05	0.06
11:31	11:36	308	225.5	69.0	7.7	6.17	0.06	0.01
11:36	11:36	8	61.2	0.6	0.4	6.25	0.02	0.01
11:36	11:38	68	107.1	47.9	11.4	6.29	0.05	0.01
11:38	11:38	7	64.1	0.6	0.4	6.35	0.01	0.01
11:38	11:38	4	60.5	1.4	1.3	6.31	0.02	0.02
11:38	11:44	392	203.2	78.6	7.8	6.47	0.08	0.01
11:44	11:45	18	60.2	0.7	0.4	6.46	0.03	0.01
11:45	11:46	74	55.5	2.1	0.4	6.42	0.04	0.01
11:46	11:50	235	194.0	85.7	10.9	6.35	0.04	0.01
11:50	11:50	13	64.6	1.0	0.5	6.34	0.02	0.01
11:50	11:53	162	54.2	3.1	0.4	6.31	0.07	0.01
Emissions > 63 PPM		3905	193.8			5.79		
Emissions < 63 PPM		1658	44.4			5.53		
All Emissions		5563	149.3			5.71		

70.2 % of time spent spraying, 10:12 - 11:53 AM
 Outlier, from period at beginning of spraying.

Table C-6. THC Analyzer Results from November 4, 1992, Third Period of Spraying

November 4, 1992		Elapsed Time (seconds)	INLET THC (ppm)			OUTLET THC (ppm)		
Start Time	End Time		Average	Population Std. Dev.	95% Conf. Interval	Average	Population Std. Dev.	95% Conf. Interval
12:19	12:32	739	11.5	5.8	0.4	6.10	0.17	0.01
12:32	12:34	123	173.3	57.0	10.1	5.92	0.04	0.01
12:34	12:34	10	69.6	3.1	2.0	5.90	0.05	0.04
12:34	12:34	6	54.6	3.7	3.0	5.87	0.02	0.01
12:34	12:39	285	156.9	66.8	7.8	5.87	0.04	0.01
12:39	12:39	28	73.8	7.8	2.9	5.84	0.04	0.02
12:39	12:39	4	60.9	1.2	1.2	5.87	0.03	0.03
12:39	12:47	476	27.1	5.7	0.5	5.87	0.04	0.00
12:47	12:48	33	136.0	42.9	14.7	5.93	0.04	0.01
12:48	12:48	3	64.1	1.0	1.2	5.94	0.01	0.01
12:48	12:48	4	58.3	2.4	2.3	5.92	0.04	0.04
12:48	12:54	347	176.8	68.1	7.2	6.01	0.07	0.01
12:54	12:56	152	37.2	6.3	1.0	6.13	0.04	0.01
12:56	13:05	518	32.7	3.8	0.4	6.41	0.14	0.01
13:05	13:10	312	204.0	73.9	8.2	6.83	0.10	0.01
13:10	13:12	105	43.3	4.6	0.9	6.97	0.04	0.01
13:12	13:15	177	185.6	60.3	8.9	7.05	0.04	0.01
13:15	13:16	69	47.2	4.3	1.0	7.16	0.04	0.01
13:16	13:19	201	188.0	68.6	9.5	7.24	0.08	0.01
13:19	13:20	38	55.4	2.4	0.8	7.30	0.04	0.01
13:20	13:25	283	186.3	59.9	7.0	7.30	0.05	0.01
13:25	13:25	27	46.6	4.5	1.7	7.35	0.04	0.01
13:25	13:29	218	200.9	69.3	9.2	7.46	0.07	0.01
13:29	13:30	45	50.2	4.2	1.3	7.58	0.04	0.01
13:30	13:34	264	210.2	75.0	9.0	7.72	0.12	0.02
13:34	13:34	6	61.5	0.7	0.5	7.93	0.02	0.01
13:34	13:34	7	64.4	0.9	0.6	7.95	0.03	0.02
13:34	13:38	211	44.3	5.9	0.8	8.07	0.10	0.01
13:38	13:42	273	221.3	83.2	9.8	8.18	0.06	0.01
13:42	13:46	237	46.5	7.0	0.9	8.27	0.04	0.01
13:46	13:52	347	155.2	66.2	7.0	8.26	0.04	0.00
13:52	13:54	103	46.2	6.9	1.3	8.28	0.04	0.01
13:54	14:00	370	144.8	64.6	6.6	8.28	0.04	0.00
14:00	14:00	11	52.8	5.5	3.2	8.30	0.04	0.02
14:00	14:04	254	35.9	3.3	0.4	8.39	0.08	0.01
14:04	14:08	206	218.3	76.7	10.5	8.37	0.04	0.01
14:08	14:15	416	40.0	8.0	0.8	8.44	0.09	0.01
Emissions	> 63 PPM	3487	182.0			7.30		
Emissions	< 63 PPM	2266	37.5			7.05		
All	Emissions	5753	125.0			7.20		

60.6 % of time spent spraying, 12:19 - 14:15

Outlier, from periods at beginning and end of spraying.

Table C-7. THC Analyzer Results from November 5, 1992, First Period of Spraying

November 5, 1992		Elapsed Time (seconds)	INLET THC (ppm)			OUTLET THC (ppm)		
Start Time	End Time		Average	Population Std. Dev.	95% Conf. Interval	Average	Population Std. Dev.	95% Conf. Interval
8:29	8:37	467	148.0	66.1	6.0	7.41	0.30	0.03
8:37	8:37	3	61.2	0.7	0.8	6.99	0.04	0.04
8:37	8:37	5	63.2	0.5	0.4	6.97	0.01	0.01
8:37	8:38	26	55.7	3.6	1.3	6.98	0.02	0.01
8:38	8:38	11	65.0	2.1	1.3	6.95	0.03	0.02
8:38	8:38	41	51.2	6.9	2.1	6.90	0.03	0.01
8:38	8:46	440	163.8	64.6	6.0	6.73	0.06	0.01
8:46	8:49	165	46.3	5.1	0.8	6.66	0.03	0.01
8:49	8:55	386	154.6	77.1	7.7	6.83	0.15	0.02
8:55	8:55	5	58.7	1.5	1.3	7.03	0.02	0.02
8:55	8:55	6	65.2	2.5	2.0	7.04	0.02	0.02
8:55	8:56	41	52.9	3.7	1.1	7.06	0.03	0.01
8:56	8:56	3	64.0	0.7	0.8	7.12	0.02	0.02
8:56	8:56	10	60.2	1.3	0.9	7.09	0.03	0.02
8:56	8:58	113	48.3	4.4	0.8	7.14	0.04	0.01
8:58	9:03	309	190.1	69.7	7.8	7.24	0.05	0.01
9:03	9:03	5	61.9	0.3	0.3	7.27	0.02	0.02
9:03	9:03	12	65.2	1.4	0.8	7.28	0.02	0.01
9:03	9:10	398	39.8	7.2	0.7	7.25	0.07	0.01
9:10	9:14	241	180.1	76.7	9.7	6.97	0.09	0.01
9:14	9:14	10	58.6	2.1	1.3	6.90	0.02	0.01
9:14	9:14	7	64.8	1.6	1.2	6.87	0.02	0.02
9:14	9:15	14	57.8	3.1	1.6	6.88	0.03	0.01
9:15	9:17	134	43.2	8.6	1.4	6.86	0.05	0.01
9:17	9:23	391	184.6	58.8	5.8	6.75	0.04	0.01
9:23	9:27	227	45.1	5.5	0.7	7.69	0.80	0.11
9:27	9:32	318	163.4	76.1	8.4	9.74	0.11	0.01
9:32	9:32	3	60.9	0.6	0.7	9.75	0.03	0.04
9:32	9:33	28	59.3	2.6	1.0	10.17	0.24	0.09
9:33	9:33	7	64.4	1.3	1.0	10.72	0.09	0.06
9:33	9:33	4	61.2	0.8	0.8	10.94	0.09	0.09
9:33	9:33	9	65.7	2.1	1.4	11.11	0.11	0.07
9:33	9:35	83	45.8	4.6	1.0	10.97	0.31	0.06
9:35	9:42	438	147.7	62.0	5.8	10.89	0.37	0.04
9:42	9:42	6	61.2	1.1	0.8	9.92	0.02	0.02
9:42	9:43	41	72.5	6.3	1.9	9.89	0.04	0.02
9:43	9:43	16	54.7	4.7	2.3	10.09	0.04	0.03
9:43	9:49	373	140.6	72.2	7.3	8.77	0.69	0.07
9:49	9:49	4	60.1	0.5	0.5	7.85	0.03	0.03
9:49	9:50	18	67.9	4.5	2.1	7.81	0.03	0.01
9:50	9:50	13	68.7	2.5	1.3	7.77	0.04	0.03
9:50	9:50	4	67.3	2.8	2.7	7.71	0.01	0.01
9:50	9:50	5	59.8	1.9	1.6	7.67	0.03	0.03
9:50	9:50	4	64.6	0.5	0.5	7.70	0.01	0.01
9:50	9:50	3	59.4	1.3	1.4	7.68	0.04	0.04
9:50	9:50	4	67.1	0.9	0.9	7.64	0.01	0.01
9:50	9:50	3	61.2	1.2	1.3	7.64	0.01	0.01
9:50	9:51	24	67.8	2.2	0.9	7.60	0.03	0.01
9:51	9:51	3	64.3	1.4	1.6	7.59	0.03	0.03
9:51	9:51	5	67.9	3.0	2.7	7.56	0.04	0.03
9:51	9:51	6	59.7	1.4	1.2	7.53	0.01	0.01
9:51	9:51	3	61.5	0.8	0.9	7.50	0.04	0.04
9:51	9:51	3	64.5	1.0	1.2	7.49	0.03	0.03
9:51	9:51	4	60.4	1.1	1.1	7.48	0.02	0.02
9:51	9:51	4	60.7	1.4	1.3	7.47	0.02	0.02
9:51	9:52	20	58.3	2.1	1.0	7.42	0.04	0.02

(Continued)

Table C-7 Continued

November 5, 1992		Elapsed Time (seconds)	INLET THC (ppm)			OUTLET THC (ppm)		
Start Time	End Time		Average	Population Std. Dev.	95% Conf. Interval	Average	Population Std. Dev.	95% Conf. Interval
9:52	9:52	4	59.4	2.1	2.1	7.36	0.03	0.03
9:52	9:54	131	53.6	3.8	0.6	7.30	0.04	0.01
9:54	9:54	23	67.8	3.5	1.4	7.13	0.03	0.01
9:55	9:55	42	58.9	3.0	0.9	7.02	0.04	0.02
9:55	10:05	599	32.8	7.4	0.6	6.34	0.33	0.03
Emissions > 63 PPM		3565	156.5			7.97		
Emissions < 63 PPM		1561	47.0			7.49		
All Emissions		5126	123.1			7.82		

69.5 % of time spent spraying, 8:29 - 10:05 AM

Outlier, from period at end of spraying.

Table C-8. THC Analyzer Results from November 5, 1992, Second Period of Spraying

November 5, 1992		Elapsed Time (seconds)	INLET THC (ppm)			OUTLET THC (ppm)		
Start Time	End Time		Average	Population Std. Dev.	95% Conf. Interval	Average	Population Std. Dev.	95% Conf. Interval
10:11	10:16	281	15.6	2.2	0.3	5.42	0.13	0.02
10:16	10:20	258	182.8	67.9	8.3	5.20	0.04	0.01
10:20	10:20	13	69.0	2.2	1.3	5.13	0.02	0.01
10:20	10:20	5	59.7	1.1	1.0	5.13	0.03	0.03
10:20	10:20	5	68.7	3.6	3.1	5.11	0.02	0.02
10:20	10:23	162	32.5	9.7	1.5	5.09	0.04	0.01
10:23	10:24	50	136.8	46.3	12.9	5.02	0.03	0.01
10:24	10:24	5	60.9	0.9	0.8	4.98	0.01	0.01
10:24	10:25	28	53.8	5.2	2.0	5.00	0.04	0.01
10:25	10:28	228	191.1	58.9	7.7	4.96	0.03	0.00
10:28	10:28	4	61.1	0.4	0.4	4.93	0.01	0.01
10:28	10:28	6	66.6	1.9	1.5	4.97	0.04	0.03
10:28	10:29	18	55.5	4.6	2.1	4.96	0.04	0.02
10:29	10:29	4	63.7	0.7	0.7	4.94	0.02	0.02
10:29	10:34	282	36.7	6.9	0.8	4.94	0.05	0.01
10:34	10:35	87	119.2	53.4	11.2	4.90	0.03	0.01
10:35	10:35	3	59.9	0.3	0.3	4.94	0.02	0.03
10:35	10:35	3	66.2	1.7	2.0	4.94	0.03	0.03
10:35	10:35	3	59.4	1.5	1.7	4.93	0.02	0.02
10:35	10:42	418	172.4	85.9	8.2	4.98	0.06	0.01
10:42	10:48	326	38.6	6.7	0.7	5.02	0.04	0.01
10:48	10:52	253	180.9	75.1	9.3	4.86	0.05	0.01
10:52	10:52	3	61.9	0.6	0.7	--	--	--
10:52	10:52	8	68.8	2.0	1.3	--	--	--
10:52	10:54	112	44.3	4.7	0.9	4.77	0.04	0.01
10:54	11:02	484	165.9	72.2	6.4	4.75	0.04	0.00
11:02	11:02	5	59.8	1.2	1.0	4.86	0.01	0.01
11:02	11:03	83	41.2	6.3	1.3	4.84	0.03	0.01
11:03	11:04	13	65.8	2.2	1.3	4.87	0.04	0.02
11:04	11:13	570	32.8	5.9	0.4	4.79	0.05	0.00
11:13	11:14	36	142.6	54.5	17.8	4.70	0.02	0.01
11:14	11:14	23	53.6	4.6	1.9	4.71	0.03	0.01
11:14	11:14	18	93.0	25.0	11.5	4.69	0.03	0.01
11:14	11:15	4	61.2	0.7	0.6	4.69	0.03	0.03
11:15	11:15	3	61.5	0.4	0.5	4.67	0.02	0.02
11:15	11:15	25	48.2	4.6	1.8	4.67	0.02	0.01
11:15	11:21	343	192.3	76.2	8.0	4.62	0.05	0.01
11:21	11:21	8	56.1	3.0	2.1	4.52	0.02	0.02
11:21	11:21	3	64.0	0.9	1.0	4.52	0.01	0.01
11:21	11:24	200	37.6	5.7	0.8	4.57	0.04	0.01
11:24	11:25	45	120.9	38.8	11.4	--	--	--
11:25	11:26	42	51.8	5.1	1.5	--	--	--
11:26	11:33	440	156.9	79.6	7.4	4.43	0.11	0.01
11:33	11:37	211	32.2	6.3	0.9	4.31	0.04	0.01
11:37	11:37	24	123.5	47.8	19.1	4.31	0.03	0.01
11:37	11:37	14	97.7	24.0	12.5	4.31	0.04	0.02
11:37	11:39	82	45.4	7.2	1.5	4.30	0.03	0.01
11:39	11:45	362	214.5	65.0	6.7	4.27	0.04	0.01
11:45	11:45	8	71.4	6.3	4.4	4.25	0.02	0.02
11:45	11:49	251	37.5	5.8	0.7	4.18	0.06	0.01
Emissions	> 63 PPM	3123	172.7			4.73		
Emissions	< 63 PPM	2207	37.6			4.78		
All	Emissions	5330	116.8			4.76		

58.6 % of time spent spraying, 10:11 - 11:49 AM

- Outlier, from period at beginning or end of spraying.
- ** Data lost due to flame out of FID in outlet THC analyzer.

Table C-9. THC Analyzer Results from November 5, 1992, Third Period of Spraying

November 5, 1992		Elapsed Time (seconds)	INLET THC (ppm)			OUTLET THC (ppm)		
Start Time	End Time		Average	Population Std. Dev.	95% Conf. Interval	Average	Population Std. Dev.	95% Conf. Interval
12:19	12:33	763	6.6	3.4	0.3	3.34	0.10	0.01
12:33	12:33	26	135.5	43.5	16.7	3.18	0.04	0.01
12:33	12:34	11	53.2	5.3	3.1	3.17	0.02	0.01
12:34	12:38	245	168.1	71.6	8.9	3.13	0.04	0.01
12:38	12:42	245	25.7	7.4	0.9	3.10	0.03	0.00
12:42	12:47	344	142.9	68.8	7.2	3.16	0.04	0.00
12:48	12:48	4	67.4	3.0	3.0	3.16	0.03	0.03
12:48	12:48	9	65.4	2.1	1.3	3.14	0.02	0.01
12:48	12:48	5	60.4	1.4	1.3	3.14	0.02	0.02
12:48	12:48	4	64.8	0.4	0.4	3.16	0.02	0.02
12:48	12:48	4	60.4	0.9	0.9	3.16	0.04	0.04
12:48	12:48	9	58.4	2.2	1.4	3.15	0.03	0.02
12:48	12:53	307	84.9	8.6	1.0	3.15	0.04	0.00
12:53	12:53	8	65.4	2.4	1.7	3.09	0.02	0.02
12:53	12:54	60	68.1	2.7	0.7	3.08	0.03	0.01
12:54	12:54	4	60.5	0.8	0.8	3.06	0.02	0.02
12:55	12:55	4	60.4	0.9	0.9	3.04	0.02	0.02
12:55	12:55	6	61.5	0.7	0.5	3.07	0.03	0.02
12:55	12:55	10	65.7	1.7	1.1	3.07	0.03	0.02
12:55	12:56	66	48.8	4.7	1.2	3.08	0.03	0.01
12:56	12:57	36	141.2	53.6	17.5	3.09	0.04	0.01
12:57	12:57	3	60.1	2.0	2.1	3.15	0.03	0.03
12:57	13:00	217	204.2	70.7	9.4	3.06	0.03	0.00
13:00	13:06	365	40.9	4.8	0.4	3.09	0.04	0.00
13:06	13:11	271	194.2	62.9	7.5	3.25	0.08	0.01
13:11	13:12	90	48.0	5.1	1.1	3.40	0.04	0.01
13:12	13:13	50	116.4	43.6	12.1	3.44	0.03	0.01
13:13	13:17	247	188.7	58.4	7.2	3.61	0.09	0.01
13:17	13:18	58	48.8	4.8	1.3	3.72	0.03	0.01
13:33	13:34	114	116.1	55.6	10.2	3.99	0.01	0.00
13:34	13:38	225	34.9	5.5	0.7	4.05	0.04	0.01
13:38	13:50	723	144.8	73.6	5.4	4.13	0.07	0.01
13:50	13:54	252	36.9	15.7	2.0	3.98	0.06	0.01
13:54	13:59	292	163.8	59.6	6.8	3.88	0.02	0.00
13:59	14:03	223	35.9	10.7	1.4	3.93	0.01	0.00
14:03	14:07	262	164.5	55.7	6.7	3.96	0.02	0.00
14:07	14:14	370	27.7	7.2	0.7	3.89	0.02	0.00
Emissions > 63 PPM		3229	151.6			3.57		
Emissions < 63 PPM		1570	37.8			3.54		
All Emissions		4799	114.4			3.56		

- * 67.3 % of time spent spraying, 12:19 - 2:14 PM
- * Outlier, from period at beginning or end of spraying.
- ** THC data lost due to power failure.