Standard Operating Procedure for Methanalyzer-100
DRAFT

U. S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Monitoring and Quality Assurance Group

A.1. Introduction

Formaldehyde (HCHO) is a colorless, strong smelling gas. The primary sources of HCHO in ambient air are produced directly and indirectly from combustion processes. Direct emission sources include industry (i.e., manufacture of resins), stationary combustion (i.e., power plant), biomass burning, exhaust from diesel and gasoline powered vehicles. Secondary sources of HCHO are derived from hydrocarbons photoxidation products and atmospheric photochemical oxidation by sunlight resulting in hydrocarbons or other formaldehyde precursors that have been released during combustion.

Ambient atmospheric concentrations of formaldehyde occur around 0.6 ppbv (Lowe and Schmidt, 1983). The health effects of concentrated atmospheric HCHO include eye irritation, carcinogen (cancer causing agent) in laboratory animals and possibly in humans and respiratory problems. In addition, concentrated atmospheric HCHO is an important agent that forms ozone, because the oxygen in the HCHO molecule allows Nitrogen Oxide (NO) to form Nitrogen Dioxide (NO_2) without breaking down ozone, thus ozone accumulates. Because of all these effects, a variety of instruments have been developed to monitor and determine HCHO concentrations; one of which is the Methanalyzer-100.

A.2. Theory of Operation

For sensitivity and specificity measurements to determine formaldehyde concentration in ambient air, 2,4-pentanedione is the method of choice. The 2,4-pentanedione and ammonium acetate serve as sources of Ammonia (NH_3) and as a buffering agent for determining formaldehyde concentration as shown in the equation below:

$$2CH_3COCH_2CO_3 + HCHO + NH_3 \longrightarrow CH_3COC{=}C(CH)_3\text{-}NHC(CH)_3{=}C(CH_2)COCH_3^*$$

2,4-pentanedione Formaldehyde Ammonia

3,5-diacetyle-1,4-dihydrolutidine (Fluorescent product)

Fluorescent excitation and emission of 3,5-diacetyle-1,4-dihydrolutidine occurs at 412 nm and 410 nm respectively. Water is used as the carrier through a six port injection valve. With the valve in LOAD position (knob rotated counter clockwise) a sample air is loaded through the system to the Diffusion Scrubber unit. The sample air moves countercurrent to the water flow and passes around a Nafion®membrane inside the Diffusion Scrubber so that any HCHO in the sample has a chance to collide with and be retained by water held near the outer tube surface. The retained HCHO permeates through the Nafion®membrane and diffuses into the water stream. Ammonium acetate and acetylacetone reagents merged at an equal flow rate and mix at a tee connector. The water stream including HCHO mixes with the reagents before entering a reactor chamber, which is 500 μL in volume and maintained at 60-90^o C.

The water stream including HCHO and the mixed reagents form a fluorescent product, which is detected by fluorescence detector and proceeds through a waste line located on the back panel to the waste bottle.

A.3 Hazards and Material Safety

Use of liquid formaldehyde:

- Wear protection equipment (e.g. gloves and goggles).
- Immediately remove any clothing that comes in contact with the product.
- In case of skin contact immediately wash with water and soap and rinse thoroughly.
- In case of eye contact rinse opened eye for several minutes with water. Then consult a doctor.
- Store in tightly closed containers in a cool, dry place away from oxidizing agents.

Use Of Ammonium Acetate:

- Avoid skin contact with ammonium acetate.
- Wash contaminated skin with soap and water.
- Wear protective gloves.
- Wear impact resistance eye protection with side shields or goggles.
- If Ammonium Acetate is spilled, remove all ignition sources, wash and clean up the area.
- Store Ammonium Acetate in tightly closed containers in a cool, well-ventilated area away from moisture.

Use of Methanol

- In case of spill eliminate sources of ignition, contain and recover liquid if possible and don't allow spill to enter into sewers or waterways.
- Store in a cool, dry, well-ventilated area suitable for flammable liquids.
- Keep container closed when is not in use.

Use of Acetic Acid

- In case of a spill or leak, don't touch the spill material, stop the leak if it is possible to do so without risk and remove all sources of heat and ignition.
- Store in tightly sealed container and label it.

A.4 Instrument Precautions

When operating this instrument, the following precautions should be observed:

- Place the instrument on a firm horizontal surface, free from vibration, temperature fluctuation and direct sunlight. The instrument top cover should be closed during operation, because the photomultiplier tube is very sensitive to light and external light leakage is always possible.
- Do not shut down the instrument if you intend to do so for 8 hours or less. Because the instrument is designed to run continuously.
- Prime the Diffusion Scrubber during initial startup procedure with distilled water; if any reagent gets into the Diffusion Scrubber, it will cause irreversible damage.
- For long term shutdown (more than two weeks); when you intend to flush the reactor with acetone, make sure to flush 20-25ml distilled water through the reactor by using 1mL syringe to flush out the acetone, if the acetone is not completely flushed out of the reactor it will cause irreversible damage to the detector.
- Filter the Ammonium Acetate during the reagent preparation; because undissolved salts may block the lines.
- Be sure to follow the proper shutdown sequence procedure indicated in section A.5.3.
- If a reagent or other liquid is spilled on the instrument interior, soak up with paper towels and then wipe with towels moistened with clean water.

A.5 OPERATION

A.5.1 Startup Procedure

A.5.1.1 Initial Setup

- Fill the water and reagent bottles with distilled water and appropriate reagents, then place them in the instrument where labeled.
- Prime bottle filters by removing the bottle caps with attached filters. Flush with 30mL distilled water using a syringe, or disconnect the lines that go to the bottle, close the air line fitting on bottle's cap then squeeze the bottle until water is seen coming out through the filter.
- Prime the three lines leading from the bottles to the peristaltic pump by using 30mL syringe filled with distilled water.
- Attach the color- coded fittings (green is water, yellow is Acetylacetone, purple is Ammonium Acetate).
- Prime the Diffusion Scrubber by disconnecting the water line from the Water IN port located on the back of the instrument panel. Connect the water line to the 30mL syringe filled with distilled water, and then push the 30mL syringe until water drops are seen coming from the Diffusion Scrubber Water IN port.
- Close the locking bars on the pump's Compression cams.
- Adjusting the peristaltic pump (See section A.6.1.1)

- Activate the system by turning on the main power switch located at the rear of the instrument.
- Debubble the system through FLUSH PORTS A and B located on the back panel approximately four to five times (See section A.5.1.4.1).
- Debubble the system through LIQUID INJECTION port located on the front panel approximately two to three times (See section A.5.1.4.2).
- Set the instrument up as in section A.5.1.2 indicated bellow, and then let the instrument run for approximately three to four hours to establish a baseline before sampling or cycling.

A.5.1.2 Front Panel and Display Selector

The front panel has 8 positions that should be set as followed:

Air Pump	On
Prime	Off
Source Lamp	On
Reactor Heater	On
Reactor Temperature Controller	80^{o} C
LIQUID INJECTION valve	LOAD
GAS/LIQUID valve	Gas

Diffusion Scrubber temperature Controller should be at the room temperature

The display selector has 5 positions:

Detector out, Compensated out, Zero, Flow rate and source level. The Display should be set as Detector out.

A.5.1.3 Zeroing the Instrument

Zero the instrument before start sampling or cycling to allow the instrument to establish a stable base line. This may take approximately three to four hours

- Toggle the VALVE mode button to Zero mode (CYCLE indicator off).
- After three to four hours and stable baseline established, adjust the zero by manipulating the ZERO control buttons located on the front panel to a range between 972-963 (factory zero set to 972). The Detector out should display zero or as close as possible.

A.5.1.4 Debubbling

Often present at startup, bubbles present problems for the instrument operation.

A.5.1.4.1 To Perform Debubbling of the Detector:

- Fill two 30ml syringes with Isopropanol or Methanol.
- With the peristaltic pump operating remove the caps from FLUSH PORTS A and B located on the rear panel.
- Connect the syringes to both FLUSH PORTS pushing only one syringe at the time.

- Remove the syringes and replace the caps tightly on the FLUSH PORTS.
- Repeat as required to remove the bubbles.

A.5.1.4.2 Debubbling Through LIQUID INJECTION Port

In order to perform debubbling from LIQUID INJECTION port located on the front panel:

- Use a 1ml syringe filled with Isopropanol or Methanol.
- Connect it to the LIQUID INJECTION port and turn the INJECTION VALVE to INJECT position.
- Inject Isopropanol or Methanol into the instrument.
- Wait for 5 minutes and then turn the INJECTION valve back to the LOAD position.
- Remove the syringe and replace the caps firmly on the LIQUID INJECTION port.
- Repeat as required to remove the bubbles.

A.5.2 Calibration

The instrument can be calibrated using either liquid or gas formaldehyde standards. At this time only liquid calibration is done on a routine basis. However liquid calibration will not check the gas Diffusion Scrubber. A gas calibration device using a HCHO permeation tube is being developed. Dynamic dilution of pressurized gas cylinders may also be used.

A.5.2.1 Liquid Calibration Calculation

Stock of 37% Formaldehyde solution (density = 1.083 g/ml).

Calculation (sample):

Assume we have 100g of HCHO solution.

$$37\% \text{ of the HCHO solution} = 100\text{g HCHO} \times \frac{37}{100} = 37\text{g HCHO}$$

$$\text{Mol of HCHO} = 37.0\text{g HCHO} \times \frac{1 \text{ mol HCHO}}{30.03\text{g HCHO}} = 1.232 \text{ mol HCHO}$$

$$\text{Liter solution} = 100\text{g HCHO solution} \times \frac{1 \text{ ml solution}}{1.083\text{g}} = 0.0923 \text{ L solution}$$

$$\text{Molarity (M) of HCHO} = \frac{1.232 \text{ mol HCHO}}{0.0923 \text{ L solution}} = 13.3 \text{ M}$$

1- Pipet 2.8 ml 37% HCHO solution to a one liter volumetric flask and then dilute to 1 liter with distilled water and mix well.

$13.3 \text{ M} \times 2.8 \text{ ml} = 1000 \text{ ml} \times M_2$

$M_2 = 37.3 \text{ mM}$

2- Pipet 0.75 ml of the 37.3 mM HCHO solution to a 100 ml volumetric flask and then dilute to100 ml with distilled water and mix well.

$37.3 \text{ mM} \times 0.75 \text{ ml} = 100 \text{ ml} \times M_3$

$M_3 = 280 \ \mu M$

3- Pipet 1 ml of the 280 μM HCHO solution to a 100 ml volumetric flask and then dilute to100 ml with distilled water and mix well.

$280\ \mu M \times 1\ ml = 100\ ml \times M_4$

$M_4 = 2.8\ \mu M$

4- Pipet 10.7 ml of the 2.8 μM HCHO solution to a 100 ml volumetric flask and then dilute to100 ml with distilled water and mix well.

$2.8\ \mu M \times 10.7\ ml = 100\ ml \times M_5$

$M_5 = 0.3\ \mu M$

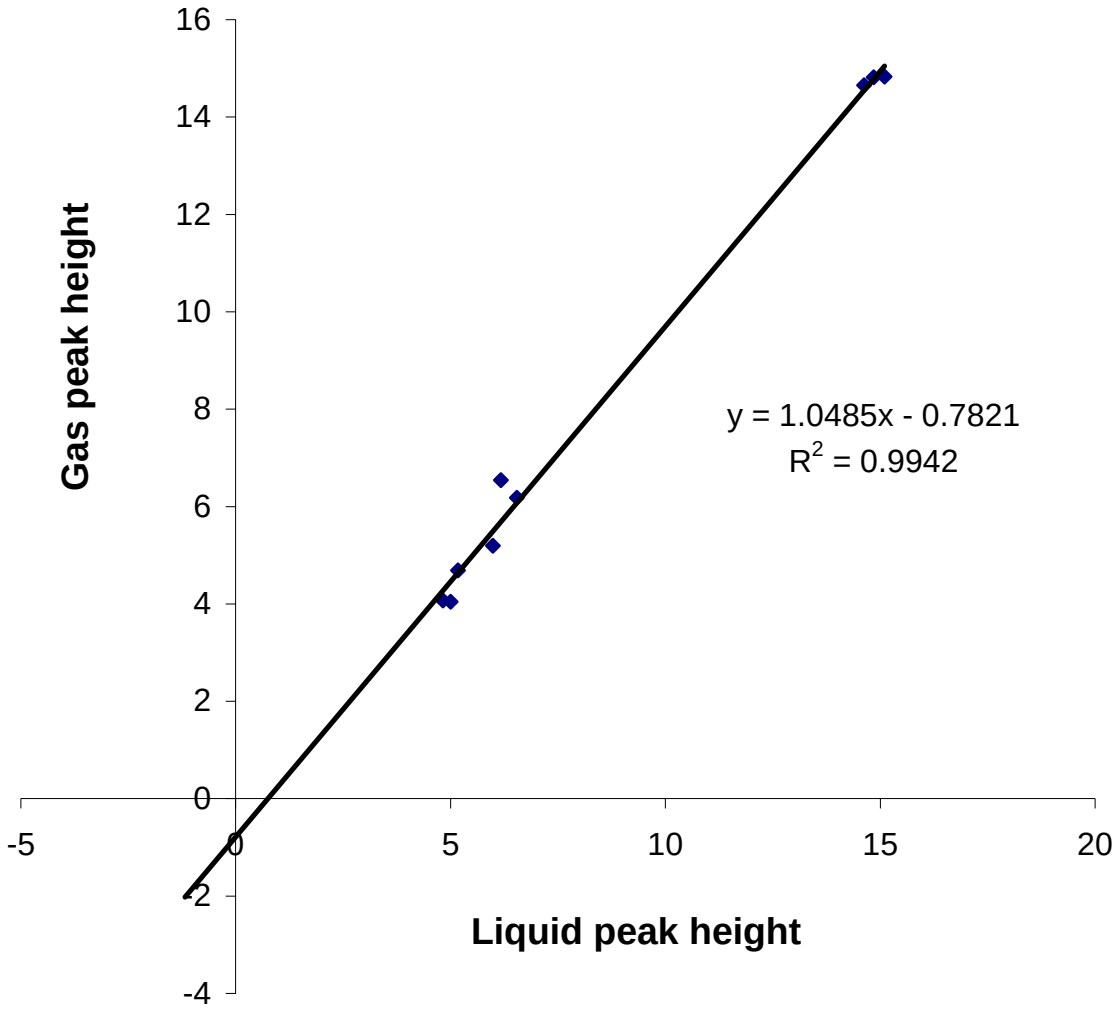
Conversion:

$$PPM = \frac{\text{mg of solute}}{\text{L of solution}}$$

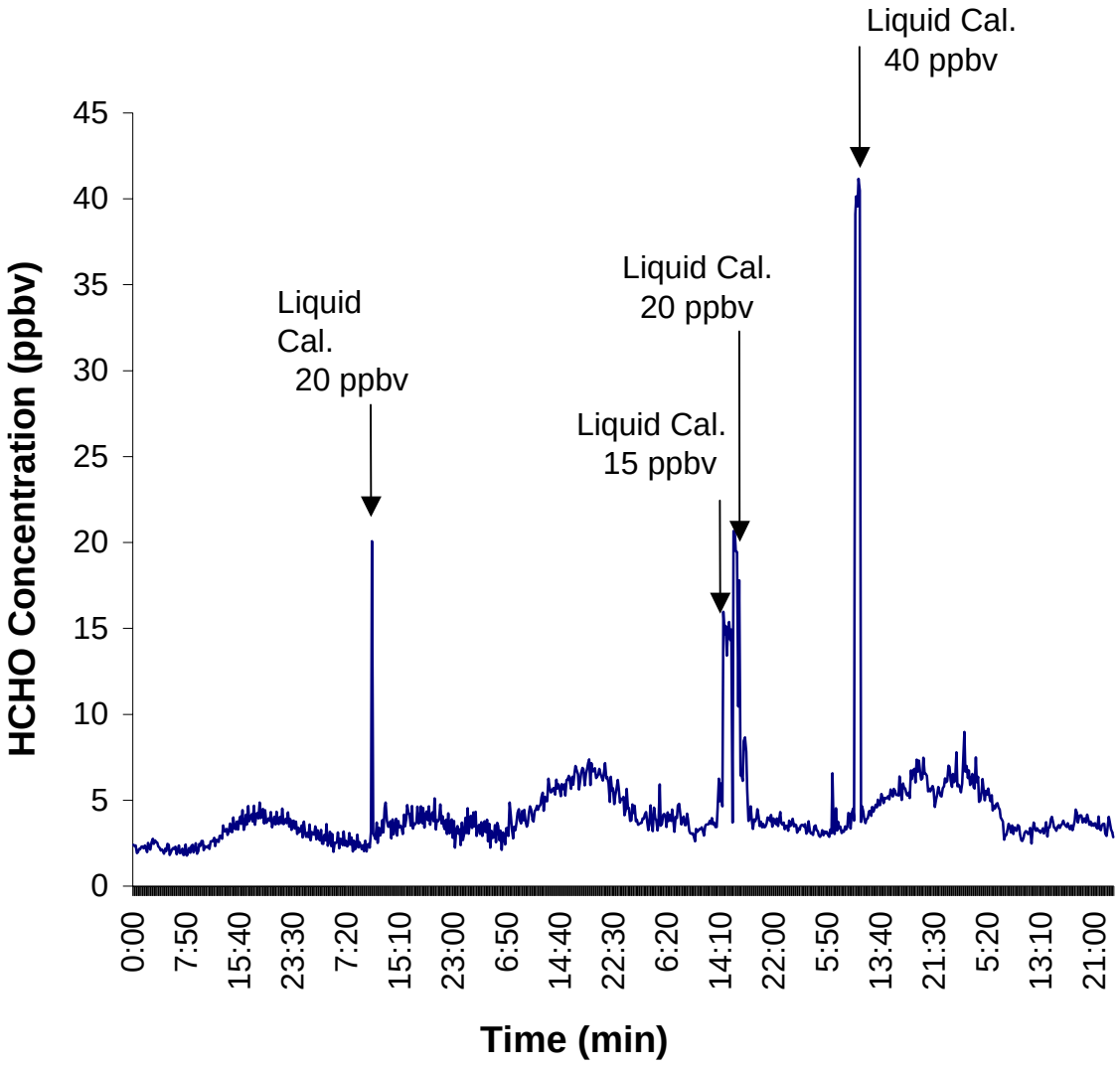
$$0.3\ \mu M\ HCHO \times \frac{10^{-6}\ M}{1\ \mu M} = 0.3 \times 10^{-6}\ M\ HCHO$$

$$0.3 \times 10^{-6}\ \frac{mol}{L}\ HCHO \times \frac{30.03\ g\ HCHO}{1\ mol\ HCHO} \times \frac{1\ mg}{1000g}$$

$= 0.009\ mg/L = 0.009\ PPM = 9\ ppb$



Gas Peak Height vs. Liquid Peak Height



HCHO Concentration (Room Air) September 20-25, 2002 (Time EST).
Liquid Calibration (15, 20 and 40 ppb) HCHO solution.

A.5.3 Shutdown

- The instrument is designed to run continuously. Make and store (via refrigerator) enough reagents to avoid shutdown every five days. To shutdown the instrument for a period less than two weeks, follow the shutdown procedure outlined below.

A.5.3.1 Shutting Down the Reactor Heater

- Press on the REACTOR HEATER switch. The red led should go off, indicating that the heater power is off.
- Wait until the reactor heater temperature reaches 40^{o} C or less before proceeding to the next step.

A.5.3.2 Water Flush

- Stop the peristaltic pump by pressing the LIQUID PUMP button; the green indictor should go off, indicating that the pump will stop.
- Remove the reagent bottles, discard any remaining reagent, rinse and fill the bottles with distilled water.
- Replace the bottles and restart the pump by pressing LIQUID PUMP button.
- Pump distilled water through the system for at least 30 minutes until the reactor temperature reaches 40^{o} C or below.

A.5.3.3 Diffusion Scrubber Shutdown

- Disconnect the water lines to and from the Diffusion Scrubber on the back of the instrument.
- Reconnect one of the lines between the IN and OUT connectors on the rear panel of the instrument.
- Use 30ml syringe filled with air to purge the carrier water from the Diffusion Scrubber. Repeat this process two times. Continue zero airflow for 15 minute.

A.5.3.4 Pump Shutdown

- Stop the Peristaltic pump by pressing the LIQUID PUMP button. The green indicator should go off.
- Release the locking bars on the pump on the compression cams.
- Unscrew the liquid lines from the water and the reagent bottles.
- Rinse out all three bottles with distilled water then dry.

A.5.3.5 Flushing the Reactor

Flushing the reactor should be done only when the instrument is shutting down and store for extended period of time (more than two weeks).

- Disconnect the fittings at the reactor.
- Flush 10-15ml Acetone through the reactor by using 1ml syringe.
- Flush 20-25ml distilled water through the reactor by using 1ml syringe.

A.5.3.6 Power Shutoff

- Turn the instrument off via the switch at the rear of the instrument.

A.5.3.7 Empty and Rinse the Waste Bottle

- Empty the waste bottle only in accordance with all Federal, State and Local laws.
- Check with your local regulatory agencies for proper disposal.

A.6 MAINTENANCE

A.6.1 Pump Tubing

- Replace the pump tubing on a routine basis (every two weeks of continuous use).
- Replace the pump tubing weekly for precise low-level measurements.
- Lubricate the pump tubing and rollers with Silicon spray lubricant.
- When replacing the tubing all three tubes should be replaced together.
- Use 0.25mm i.d. pump tubing for Ammonium Acetate and Acetylacetone.
- Use 0.51mm i.d. pump tubing for water.
- Measure 6-3/4 inches long tubing length.
- Center the pump tubing inside the cam.

A.6.1.1 Adjusting Peristaltic Pump

- Prime the tubing with distilled water; this will prevent bubbles from being introduced to the system.
- Close the tension bar on the tubing.
- Introduce a bubble to the line by unscrew the bottle fitting.
- Loosen the compression screw until the bubble stops moving.
- Tighten the compression screw until flow just begins.
- Tighten the compression screw further one full turn.
- Repeat the procedure for the other tubing lines.

A.7 TROUBLESHOUTING

Problem	Fix
There are bubbles present in the lines that go from the bottles to the peristaltic pump	❑ Check the fittings and connections on the outside and inside of the bottle's cap for leaks. ❑ Make sure that there are no loose fittings. ❑ Make sure that the fittings are not too tight. ❑ If the fittings are not sealing replace them with new ones. ❑ Check to ensure that there is sufficient amount of reagent or DI water in the bottles. ❑ Check to ensure that the bottle filters are submerged in the solution. ❑ Make sure that the bottle filters are primed properly.
Bubble coming from the Water Out located on the back panel of the instrument going through the line to the DS.	❑ Flush the DS with distilled water. ❑ Check the fittings on the Outlet Port of the DS and ensure that they are not loose. ❑ Check the fittings on the water bottle's cap and the filter and ensure that they are not loose. ❑ Check the fittings on the GAS/LIQUID valve and ensure that they are not loose. ❑ Remove the water bottle's cap with its filter and then submerge the water line without the fitting into the water bottle.

Problem	Fix
There are bubbles present from the GAS/LIQUID valve to the Diffusion Scrubber.	❑ Check all the fitting connections from the valve to the DS. Make sure there is not a loose fitting. ❑ Make sure the fittings are not too tight. ❑ If the fittings are not sealing, replace them with a new one.
Bubble coming out of the DS but not going in.	❑ Check the fitting on the Outlet Port of the DS and ensure that it is not loose. ❑ Flush the DS.
Detector out display a number close to 99.	Perform debubbling on the detector by using FLUSH PORTS A and B. (See section A.5.1.4.1).
The instrument loses signal.	❑ Check to ensure that the detector is on. ❑ Check to ensure that the AIR PUMP is on. ❑ Check to see if the reactor is on. ❑ Check to ensure that the instrument is switched to the GAS mode. ❑ Check to ensure that all the reagent bottles are pumping fluid. ❑ Change the pump tubing if they need replace.
Broad peaks.	❑ Check the pump tubing to ensure that the reagents are flowing properly through the pump.

Problem	Fix
Reagents are not flowing properly through the pump.	❑ Check and adjust the Peristaltic pump (See section A.6.1.1)

A.8 Reagents Preparation

A.8.1 Acetylacetone Preparation

- Pipette 3.2ml of Acetylacetone into 500ml volumetric flask.
- Add distilled water to make up 500ml reagent solution.
- Pour the make up solution into a storage bottle.
- Label the bottle appropriately.
- Store in a refrigerator (approximately 1 month).

A.8.2 Ammonium Acetate Preparation

- Weight 240g of Ammonium Acetate crystal in 1L beaker.
- Add distilled water until there is 450ml solution.
- Mixed until crystals are dissolved.
- Add 4.6ml Acetic acid and continue mixing.
- Add distilled water to make a total of 500ml solution.
- Filter the solution with a filter funnel and 1 L filter flask to make sure all crystals are dissolved before you put the solution into the bottle.
- Label the bottle appropriately.
- Store in a refrigerator (approximately 1 month).

A.9 Supplies

PART DESCRIPTION	VENDER	PART #	PHONE #
Pump Tubing (water)	Alpha-Omega Power Technologies	TUB38-01	(505) 341-4828
Pump Tubing (Reagents)	Alpha-Omega Power Technologies	TUB25-01	(505) 341-4828
Bottle Filter	Alpha-Omega Power Technologies	BF-01	(505) 341-4828
Clear Tubing	Zeus Technology	1EA19TW-0	1800-526-3842
Flangeless Fitting For1/16 Tubing	Global Fia	FF16N	(253) 549-2223
Barb Fittings for the Pump Tubing	Global Fia	PF-S	(253) 549-2223

A.10 Data Logger Acquisition

- From the main menu select Configuration Menu.
- Select Configuration (Data) Channel.
- Select Enter New Configuration.
- Setup four channels (Standard, two general channels and a math channel).
- The configuration fields of these channels should be set as followed:

A.10.1 Standard Channels

Instrument Name	Form
Analog Input number	01
Report Channel number	03
Volts full Scale	5
High Input	5v
Low Input	0v
High output (E. V.s)	100
Low Output	0
Units	ppbv
Based Avg. Interval Storage	10m, 5d 14h, 10m
Average #1 Interval Storage	20m, 11d 4h, 20m
Average #2 Interval Storage	40m, 22d 8h, 40m
Use Validation	N

A.10.2 General Channel (Maximum)

Instrument Name	Maxfrom
Report channel number	04
Input channel	Form
Input Average Interval	0s
Units	ppbv
Data channel type	Maximum
Result Input Status Pattern	(None)
General Val. Duration Storage	10m, 2d 9h, 30m
Ignore Input channel flag	None

A.10.3 General Channel (Minimum)

Instrument Name	Minfrom
Report channel number	02
Input channel	Form
Input Average Interval	0s
Units	ppbv
Data channel type	Minimum
Result Input Status Pattern	(None)
General Val. Duration Storage	10m, 2d 9h, 30m
Ignore Input channel flag	None

A.10.4 Math Channel

Instrument Name	Formcal
Report Channel Number	0s
Equation	Maxform - Minform
Units	ppbv
Base Avg. Interval Storage	10m, 5d 14h, 10m
Average #1 Interval Storage	10d, 0s
Average #2 Interval Storage	20d, 0s
Use Validation	N

A.11 Example Data

Figure 1: HCHO Concentration (Room Air) September 20-25, 2002 (Time EST).

Figure 2: HCHO Concentration (Room Air) September 20, 2002 (Time EST).

Figure 3: HCHO Concentration (Ambient Air) October 4, 2002 (Time EST).

Figure 4: HCHO Concentration (Ambient Air) October 15, 2002 (Time EST).

Figure 5: HCHO Concentration (Inside Trailer Air) October 16, 2002 (Time EST).

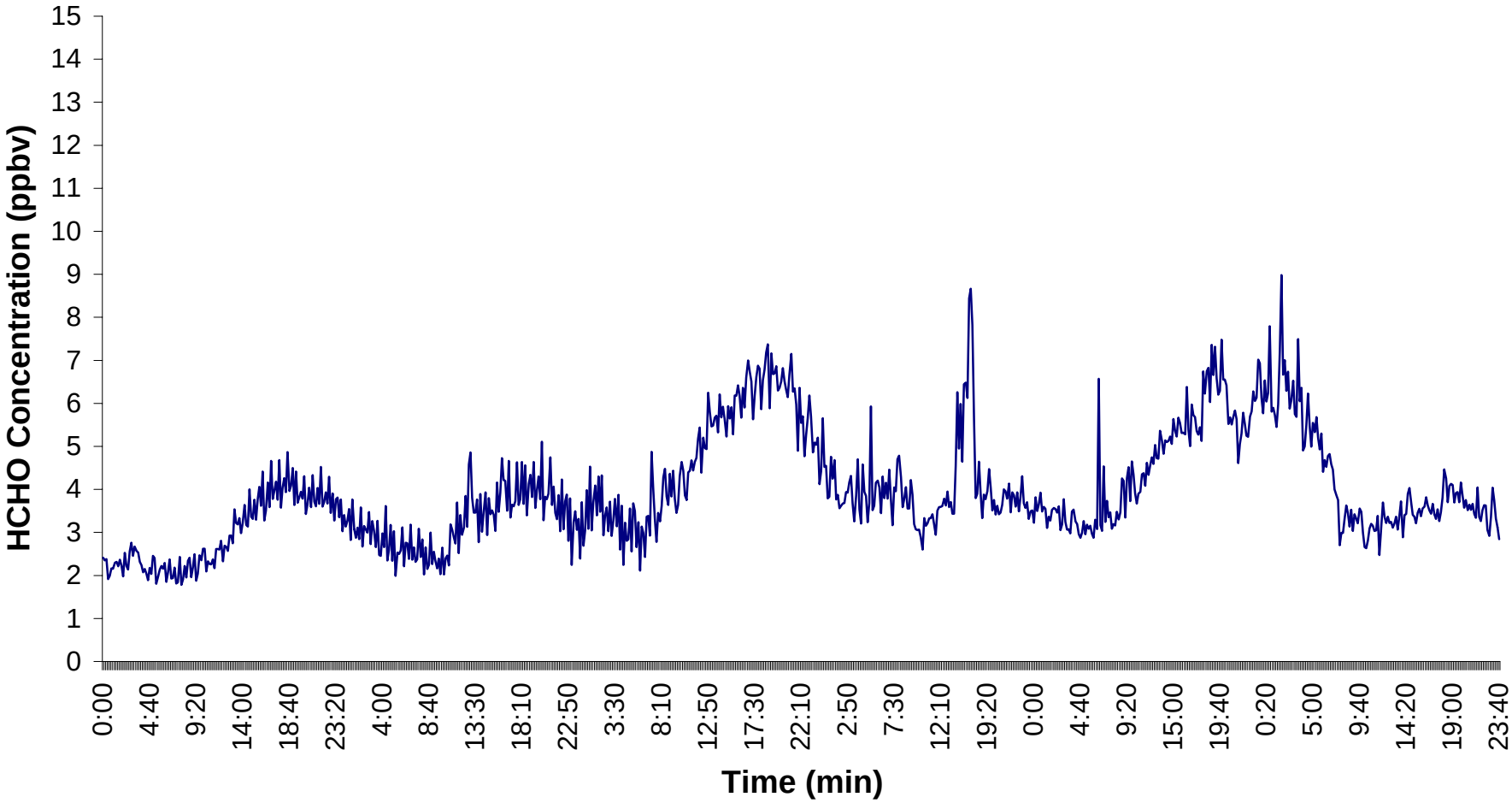


Figure 1. HCHO Concentration (Room Air) September 20 - September 25, 2002 (Time EST).

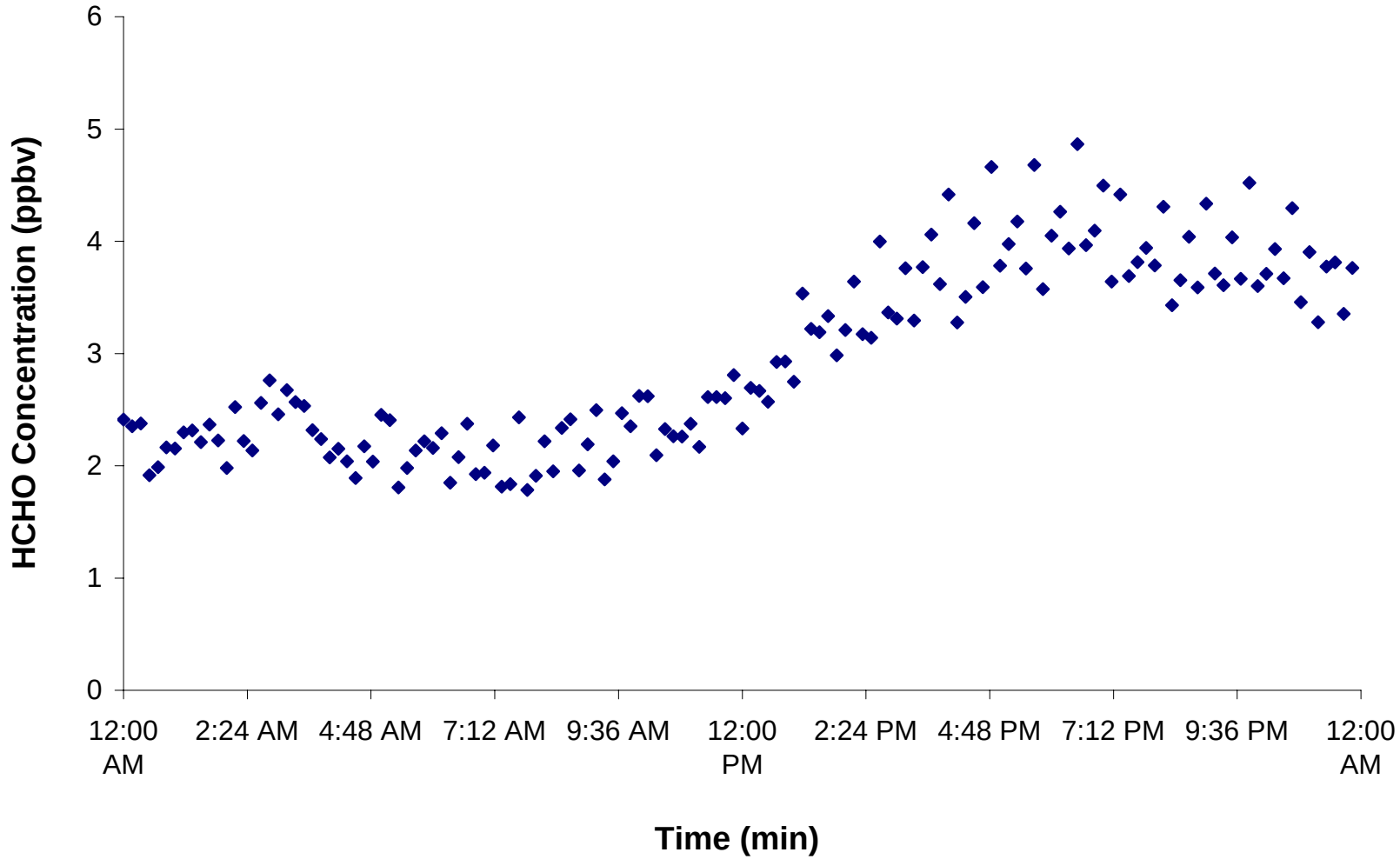


Figure 2. HCHO Concentration (Room Air) September 20, 2002 (Time EST).

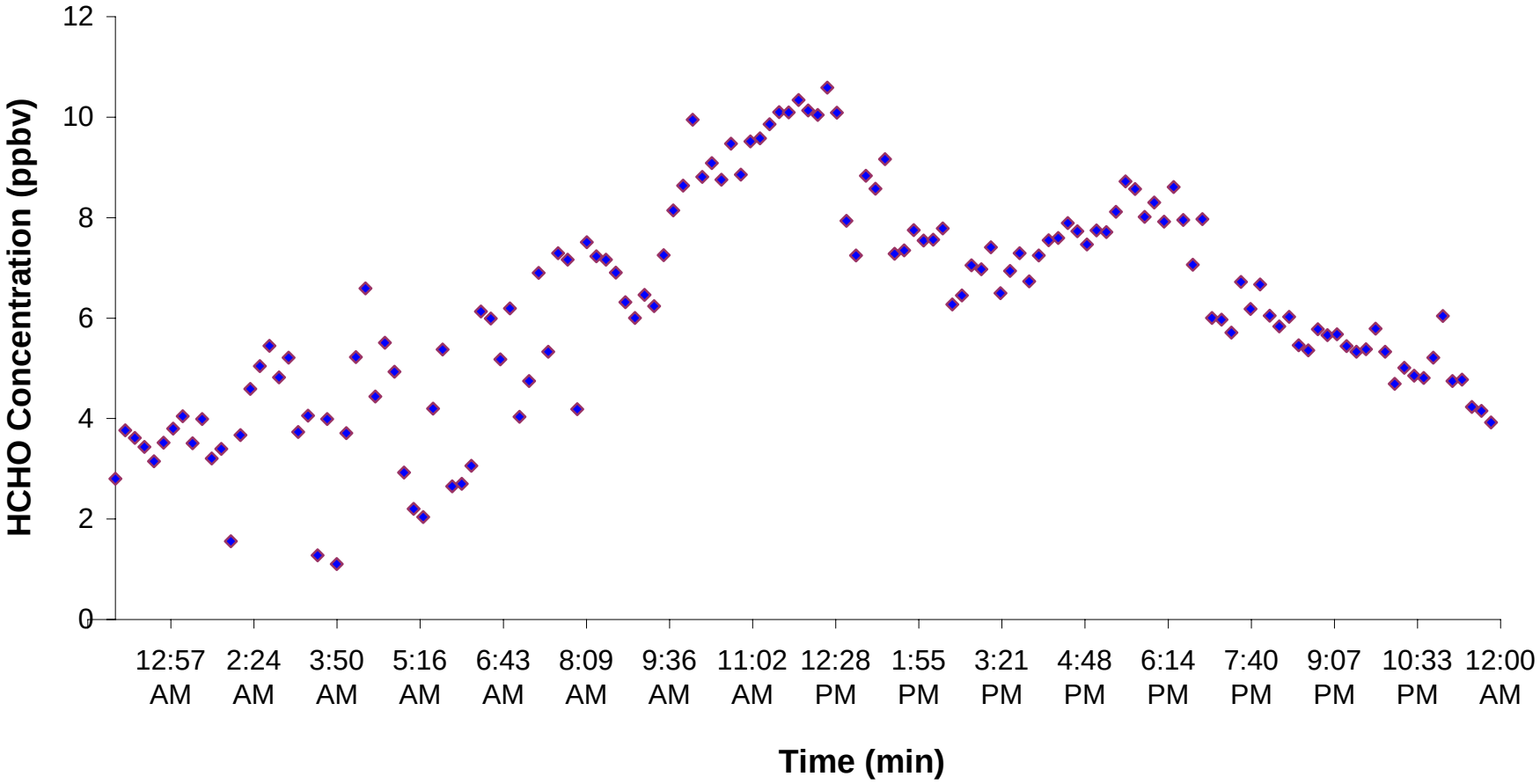


Figure 3. HCHO Concentration (Ambient Air) October 4, 2002 (Time EST).

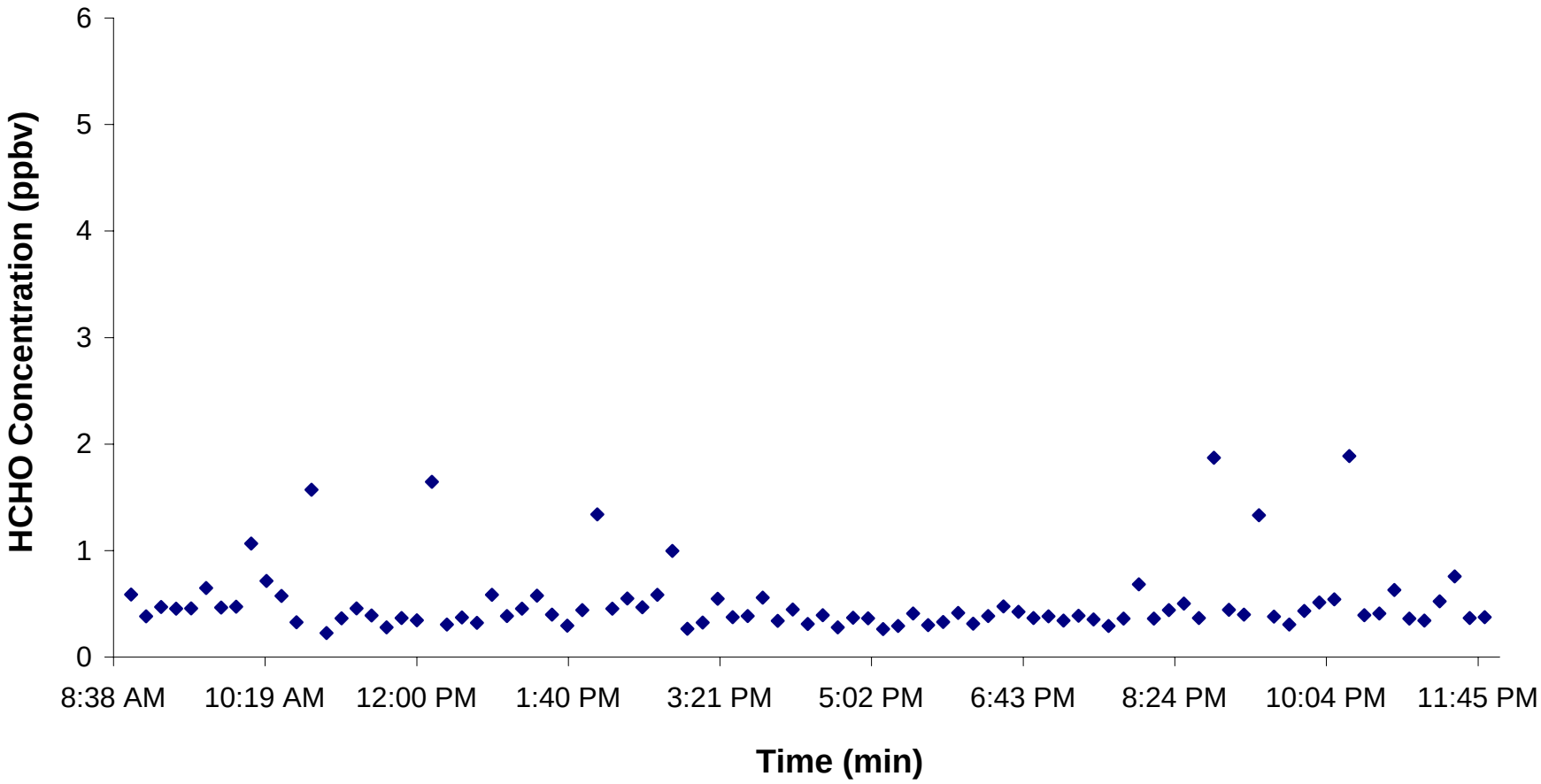


Figure 4. HCHO Concentration (Ambient Air) October 15, 2002 (Time EST).

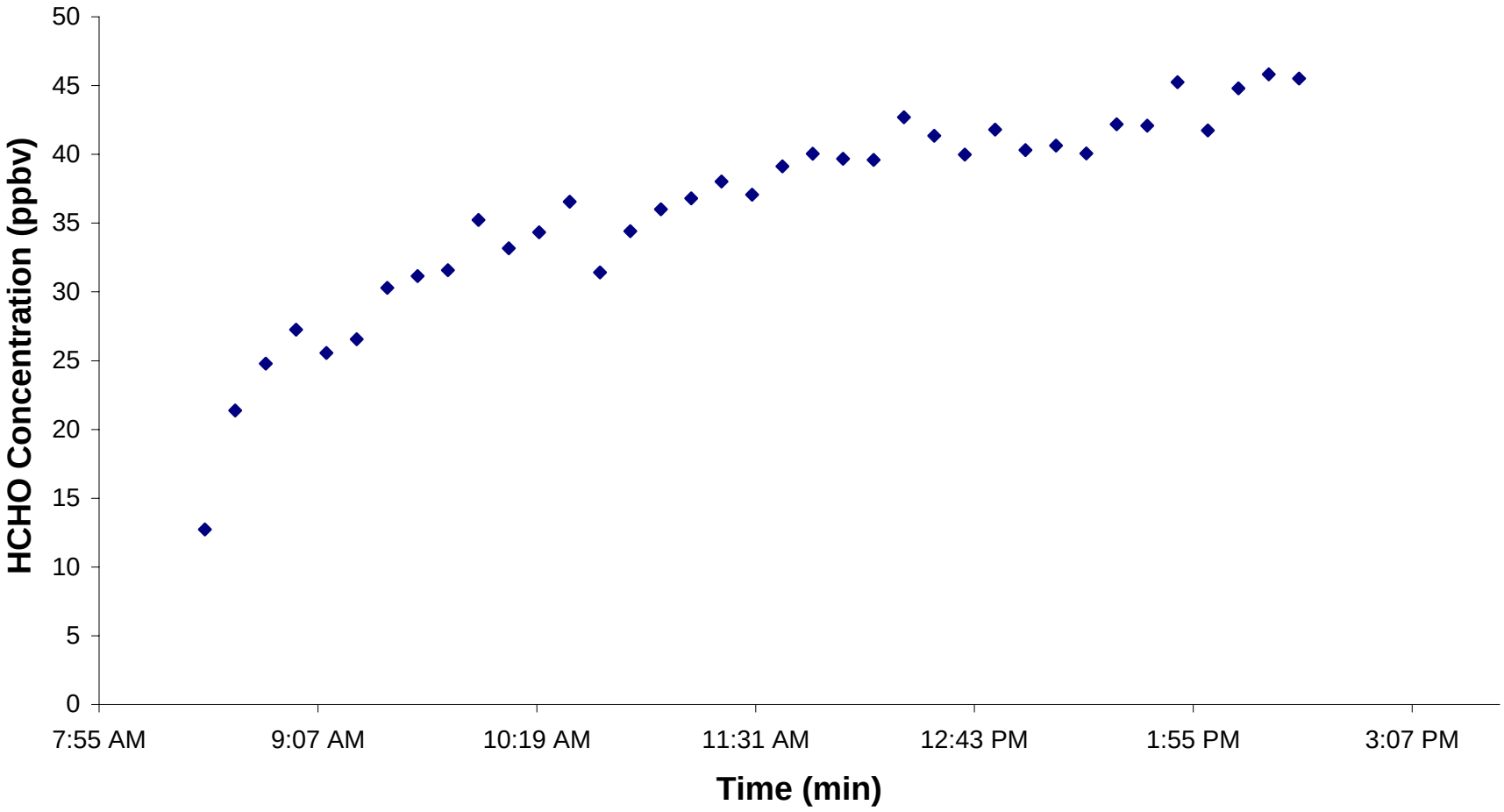


Figure 5. HCHO Concentration (Inside Trailer Air) October 16, 2002 (Time EST).