FORMALDEHYDE AIR SAMPLING

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1.0 SCOPE AND APPLICATION

The purpose of this Standard Operating Procedure (SOP) is to define the procedure for silica gel tube sampling to identify formaldehyde and other carbonyl compounds (aldehydes and ketones) in ambient air. This SOP is based US EPA Toxic Organic (TO) Compendium Method TO-11A, *Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridges Followed by High Performance Liquid Chromatography (HPLC).*

This method is applicable for the collection of time-weighted average (TWA) samples for long term (up to 24-hour sampling period) in the low parts per billion (ppb) range or short term (less than 1 hour) in the parts per million (ppm) range. Refer to Table 1, Appendix A for typical compounds that may be analyzed using this collection method.

A Quality Assurance Project Plan (QAPP) in Uniform Federal Policy (UFP) format describing the project objectives must be prepared prior to deploying for a sampling event. The sampler needs to ensure that the methods used are adequate to satisfy the quality objectives listed in the QAPP for a particular site.

The procedures in this SOP may be varied or changed as required, dependent on site conditions, equipment limitations, or other procedural limitations. In all instances, the procedures employed must be documented on a Field Change Form and attached to the QAPP. These changes must be documented in the final deliverable.

2.0 METHOD SUMMARY

A known volume of air is drawn through a tube containing silica gel coated with acidified 2,4-dinitrophenylhydrazine (2,4-DNPH) at a sampling rate of 0.5 to 1.2 liters per minute (L/min) for an appropriate period of time. Both sampling rate and time are dependent upon carbonyl concentrations in the test atmosphere.

Prior to sampling, use a tube breaker or equivalent device to remove the ends of the tube. The tube is then placed in a sample holder or placed snugly in Tygon® tubing.

As air is drawn through the tube during sampling, gases and vapors adsorb onto the surface of the silica gel. After sampling, the tubes are individually capped, labeled with identifying information and delivered to the laboratory for analysis.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

The 2,4-DNPH-coated silica gel used for sampling for formaldehyde is housed in a glass tube that has been flame sealed. The tubes most often used contain a 300-milligram (mg) front sorbent section and a 150-mg backup sorbent section. The smaller tube is 11 centimeters (cm) long with a 6-millimeter (mm) outer diameter (OD). The larger tube is 11 cm long with a 7-mm OD. Higher sampling flow rates and larger air volumes can be drawn through the larger tube thereby providing greater sensitivity. An additional tube is available containing the same coated sorbent and backup section as well as a section of potassium iodide (KI) that functions as an ozone scrubber. This tube containing an ozone scrubber is 11.5 cm with an 8-mm OD.

To preserve and store samples after sampling:

1. Place supplied plastic caps on the tube ends. Wrap tube in aluminum foil to protect from sunlight.
2. Place the sample in a small re-sealable plastic bag (Whirl-Pak® or similar).
3. All samples should be stored and shipped on ice.
4. If the sample tube must be stored for more than a week, refrigeration is recommended. The maximum recommended holding time is two weeks.

Additionally, perform work in a manner consistent with the applicable sampling method.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

Low sampling flow rates, excess sampling flow rate, temperatures below freezing, and high temperature and humidity may cause a decrease in the adsorptive capacity of the silica gel. Contaminants from the front portion of the tube may break-through or migrate to the back portion of the tube. In general, refrigeration minimizes the potential migration of adsorbed formaldehyde from the tube's front section to the rear section. Tubes or cartridges may be connected in series, or a dual bed tube may be used, to assess breakthrough.

Exposure of the DNPH-coated cartridges to direct sunlight may produce artifacts and should be avoided.

Use of the tube with built-in ozone scrubber (SKC 226-120, listed below) should not be used in high humidity environments or during precipitation. In high humidity, the ozone scrubber media will be drawn through the tube causing damage to the pumps. Subsequent analysis of these tubes will cause damage to laboratory instrumentation.

5.0 EQUIPMENT

5.1 Equipment List

- Personal Sampling Pump, SKC Universal XR Sampling Pump Model 224-PCXR8 or equivalent
- Sampling Stand, SKC Model Tripod Stand 228-506 or equivalent
- Rotameter SKC Rotameter 320-4A5, 320-4A20L or equivalent
- Formaldehyde Sampling Tube [SKC 226-119 (for flows up to 500 milliliters per minute [ml/min]), SKC 226-119-7 (for flows up to 1.2 L/min. or SKC 226-120 with built-in ozone scrubber (for flows up to 1.2 L/min.)].
- Tygon Tubing, for attaching the tube holder system to the suction side of the pump
- Protective Sleeves or plastic support tubes, to hold tubes in place
- Single or Dual Manifold Flow Controller (Optional)
- Tube Holder End, to support and seal the sampling tube within the protective sleeve
- Glass Tube Cracker
- Re-sealable Bags (Whirl-Pak or equivalent)
- Plastic End Caps
- Air Sampling Worksheets and Sample Labels
- Chain of Custody Records (hard copy from SCRIBE)
- Screwdriver Set, Universal Screwdriver Kit, SKC 224-11 or equivalent
- SCRIBE Software and Printer

5.2 Equipment Source

Tubes are commercially available from SKC, Inc. of Eighty Four, Pennsylvania. Phone: 1-800-752-8472; www.skcinc.com.

6.0 REAGENTS

This section is not applicable to this SOP.

7.0 PROCEDURES

7.1 Field Preparation

1. Determine the extent of the sampling effort, the sampling methods to be employed, and the types and amounts of equipment and supplies needed.

2. Obtain and organize the necessary sampling and monitoring equipment.

3. Decontaminate or pre-clean equipment, and ensure that it is in working order. Pre-calibrate sampling pumps as described in Section 7.2.

4. Prepare scheduling and coordinate with staff, client, and regulatory agency, if appropriate.

5. Perform a general site survey prior to site entry, in accordance with the site-specific Health and Safety Plan (HASP).

6. Use stakes, flagging tape, global positioning system (GPS), or other appropriate means to identify and mark all sampling locations. If required, the proposed locations may be adjusted based on-site access, property boundaries, and surface obstructions.

7.2 Calibration Procedures

To save time in the field, the flow rate on the sampling pumps can be pre-calibrated prior to arriving at the site using a calibrated rotameter or an electronic flow meter. The calibration of the flow rate must be checked in the field prior to use, and upon completion of sampling. Ensure that the primary or secondary calibration device has a valid calibration date. For ERT rotameters, perform calibrations following directions established in ERT SOP, *Rotameter Calibration.* If an electronic flow meter is used for calibration, ensure it has a valid calibration date. Electronic flow meters are calibrated by an outside vendor (usually by the manufacturer) and are valid for one year from calibration.

1. For flow rates above 1,000 cubic centimeters per minute (cc/min) using the SKC PCXR series pumps (model used by ERT), ensure the pump is in high-flow mode by adjusting the pump flow regulator. Please note that manufacturer and models differ in procedures for adjustments from low flow to high flow and air sampling flow rate range differs. Remove the cap cover and turn the screw clockwise (down) four to five times until it stops Figure 1, Appendix B. Do not over tighten. Assemble the calibration train as shown in Figure 2, Appendix B using an appropriate rotameter. In the high-flow mode, flow rates down to 750 cc/min are achievable, but are not

guaranteed by the manufacturer.

2. If the desired flow rate is between 5 and 500 cc/min, ensure the pump is in low flow mode by adjusting the pump flow regulator. Remove the cap cover and turn the screw counter-clockwise (up) four to five times. Assemble the calibration train as shown in Figure 3, using an electronic flow meter. In the low flow mode with a manifold, flow rates up to 750 cc/min are achievable, but are not guaranteed by the manufacturer.

3. Turn on the pump and allow it to warm up for at least one minute. Adjust the flow using the flow adjust mechanism on the manifold (if used) or on the pump itself, until the desired flow rate is achieved. This occurs when the center of the float ball on the rotameter is aligned with the rotameter's pre-calibrated flow rate value or until the electronic flow meter displays the desired flow rate value. A sticker on the rotameter should indicate this value's set point as shown in Figure 4, Appendix B.

4. If desired, affix a sticker to the manifold (if used) and pump indicating the pre-calibrated flow rate and sampling media.

5. Remove the calibration tube from the sleeve. The pump and manifold (if used) are calibrated as a unit and should not be separated until the samples have been collected. If they are separated, a new calibration will need to be performed.

6. **DO NOT** use calibration tube for sampling.

7. If desired flow rate is not achieved, check the following:

   - Verify that the pump is operational
   - Ensure that all fittings on tube housing are secure
   - Check that the tube is not cracked beyond the tip (i.e. hairline cracks).
   - Verify that both ends of the tube are open
   - Make sure that no other obstructions are present

   Ensure that Tygon tube is free of cracks, holes or kinks. As seen in the figures, the sampling train consists of (in order) the personal sampling pump and Tygon tubing connected to the protective housing holding the tube. The appropriate calibration device is affixed to the sampling inlet.

   Refer to Figures 5 and 6 respectively, for illustrations of sampling trains with a single manifold and without a manifold.

7.3 Field Operation

1. Mobilize to a clean zone and calibrate the appropriate number of sampling pumps as described in Section 7.2. If the pumps were pre-calibrated, the calibration should be checked in the same manner. Fine tuning of the flow may be necessary.

2. Calibrations may be performed in a clean area near the sampling location or at the sampling location itself.

3. Crack the silica gel tube ends using a glass tube cracker.

4. Insert the silica gel tube in the sleeve with arrow pointing in the direction of air flow (the smaller media section of the tube is used for breakthrough and is positioned nearest the sampling pump).

5. Screw the tip onto the sleeve so the tube is held in place.

6. At low flow rates (less than [<] 750 cc/min), attach the sleeve to a manifold for better flow adjustment. At high flow rates (greater than [>] 750 cc/min), silica gel tubes can sample without a manifold.

7. To set up the sampling train, attach one end of the Tygon tubing (approximately 2-feet) to the tip of the sleeve or manifold. Attach the other end of the tubing to the inlet on the sampling pump. Refer to Figures 5 and 6, Appendix B for illustrations of sampling trains. For collocated samples, a second pump may be used or for low flow rates, a dual manifold may be used.

8. Adjust time on the sampling pump to the required sample time.

9. Place the silica gel tube (Figure 7, Appendix B) in a position free from obstruction on a dowel rod or stand. Position sampling inlet in the downward facing position at a 45-degree angle to prevent intrusion of precipitation.

10. Verify calibration by connecting a rotameter or electronic flow meter with Tygon tubing and turning on the pump via the flow check button, adjust flow if needed. Record the start flow rate on the Air Sampling Worksheet. Record the serial number, barcode, or identification (ID) number of the calibration device used.

11. Record weather data (e.g., ambient temperature, barometric pressure, relative humidity, and wind direction) on the Air Sampling Worksheet or in the logbook.

12. Turn on the pump and record the start time. After one minute, verify that the pump is running and that the timer on the face of the pump is functioning. Most faults occur during the first minute of operation.

13. After setting up multiple sampling locations, return to each location to verify pump sampling operation whenever applicable and feasible.

14. After the air sampling period is complete, check the pump display screen for elapsed time and any flow or battery fault messages.

7.4 Post Operation Procedures

1. Record the total sampling and stop time on the Air Sampling Worksheet.

2. Verify flow rate by connecting a rotameter or electronic flow meter with Tygon tubing and turning on the pump. Record the end flow rate along with the calibration device's ID on the Air Sampling Worksheet.

3. Remove the silica gel tube from the sleeve.

4. Cap silica gel tubes with plastic caps immediately after sampling. Never use rubber caps.

5. Place the sample tube in a Whirl-Pak/re-sealable bag labeled with the sample ID #, total volume, and required analysis. If collocated samples have been collected, place each tube in a separate Whirl-Pak/re-sealable bag and assign a unique sample ID # to each tube.

6. Indicate all applicable information on the Air Sampling Worksheet (e.g., sample volume, ID #, location, date, and weather parameters).

7. Transfer data from Air Sampling Worksheets to SCRIBE.

8. Sample tubes must be stored in a refrigerated container or in a cooler with ice.

9. Prepare samples, including QC samples, for transport by packing them in a shipping container with ice, bubble wrap or Styrofoam pieces. Complete a Chain of Custody record in accordance with ERT SOP, *Chain of Custody Procedures*.

If there is reason to believe that the air sampling equipment may be contaminated, see ERT SOP, *Sampling Equipment Decontamination*.

8.0 CALCULATIONS

The total volume of a sample is calculated by multiplying the total sample time by the average flow rate of pre-calibration and post-calibration flow rates. The total volume for each sample is indicated on the Chain of Custody record.

9.0 QUALITY ASSURANCE/QUALITY CONTROL

Relevant information on air sampling equipment and site conditions as referenced in Section 7.0 will be recorded in a manner consistent with ERT SOP, *Logbook Documentation* or in field data sheets.

The following general QA procedures apply:

1. All data must be documented on Air Sampling Worksheets or in site logbooks and in SCRIBE.

2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the QAPP. Equipment checkout and calibration activities must occur prior to sampling/operation and must be documented.

The following specific QC activities apply:

1. Provide one field blank per sampling event or per 20 samples, whichever is greater, unless specified otherwise by the QAPP or analytical method. The field blank should be collected at the beginning of the sampling event and handled in the same manner as the sampling tube (break, seal, and transport) except that no air is drawn through it.

2. As an option, provide one trip blank per sample shipment. The trip blank should be collected at the conclusion of the sampling event, prior to shipment. It should be handled in the same manner as the sampling tube (break, seal, and transport) except that no air is drawn through it.

3. It is recommended to collect one collocated sample per sampling event or per 10 samples, whichever is greater. For the purpose of this SOP, collocated samples are two samples collected adjacent to each other during the same time period at the same flow rates. EPA TO-11A recommends that both samples be taken from the same sampling manifold. See project specific Quality Assurance Project Plan for final determination.

4. Include 5-6 lot blank tubes per manufacturer's lot used per sampling event. These tubes are taken directly from the tube box. Do not break the ends. Three of these tubes will be used by the laboratory to calculate an average media (certification) blank. Two of these tubes will be used as a blank spike/blank spike duplicate (BS/BSD) to measure accuracy and precision.

5. The back section of the cartridge must be analyzed for a minimum of 10% of the samples to assess breakthrough. However, it is highly recommended to analyze both sections of the tubes especially if high concentrations of formaldehyde is a suspected contaminant of concern.

6. It is recommended that the sampling system use a heated inlet at approximately 50 degrees Centigrade (ºC) coupled to an ozone denuder or scrubber to minimize water and ozone interference.

10.0 DATA VALIDATION

Data verification (completeness checks) must be conducted to ensure that all data inputs are present for ensuring the availability of sufficient information. This may include but is not limited to location information, start and end times, sampling method and total volume sampled. These data are essential to providing an accurate and complete final deliverable. The contractor's Task Leader (TL) is responsible for completing the UFP-QAPP verification checklist for each project.

Results of the quality control samples will be evaluated for contamination. This information will be utilized to qualify the environmental sample results accordingly with the project's data quality objectives.

11.0 HEALTH AND SAFETY

Based on Occupational Safety and Health Administration (OSHA) requirements, a site-specific health and safety plan (HASP) must be prepared for response operations under the Hazardous Waste Operations and Emergency Response (HAZWOPER) standard, 29 CFR 1910.120. Field personnel working for EPA's ERT should consult the Emergency Responder Health and Safety Manual currently located at https://response.epa.gov/_HealthSafetyManual/manual-index.htm for the development of the HASP, required personal protective equipment (PPE) and respiratory protection.

12.0 REFERENCES

SKC Inc., Operating Instructions, Universal Sample Pump (Cat. No. 224-PCXR8), Form 37717, Rev. 1302.

EPA Method TO-11A, Determination Of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed By High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology], January 1999.

ASTM Method D5197, Standard Test Method for Determination of Formaldehyde and Other Carbonyl Compounds in Air (Active Sampler Methodology), September 2010.

13.0 APPENDICES

A – Table 1
B – Figures
C – Air Sampling Worksheet

APPENDIX A
Table 1 – Example Compound List for Aldehydes/Ketones
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Table 1. Example Compound List for Aldehydes/Ketones

Analyte
2,5-Dimethylbenzaldehyde
Acetaldehyde
Acetone
Benzaldehyde
Crotonaldehyde
Formaldehyde
Glutaraldehyde
Hexaldehyde
Isobutyraldehyde/Butyraldehyde
Isovaleraldehyde
o,m,p-Tolualdehyde
Propionaldehyde
Valeraldehyde

APPENDIX B
Figures
SOP: ERT-PROC-2131-20
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FIGURE 1. Sampling Pump Regulator

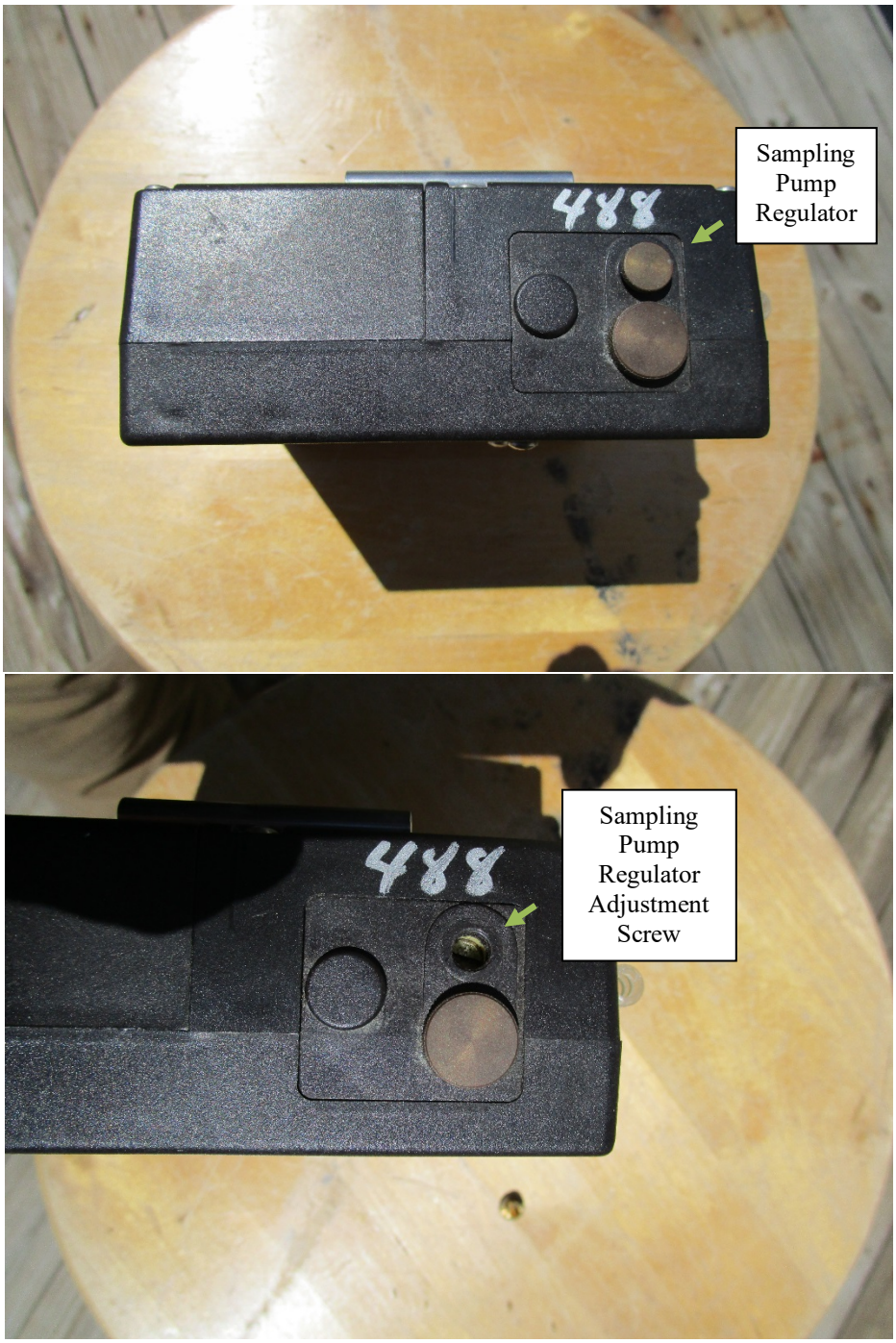


FIGURE 2. Calibration Train (No Manifold)

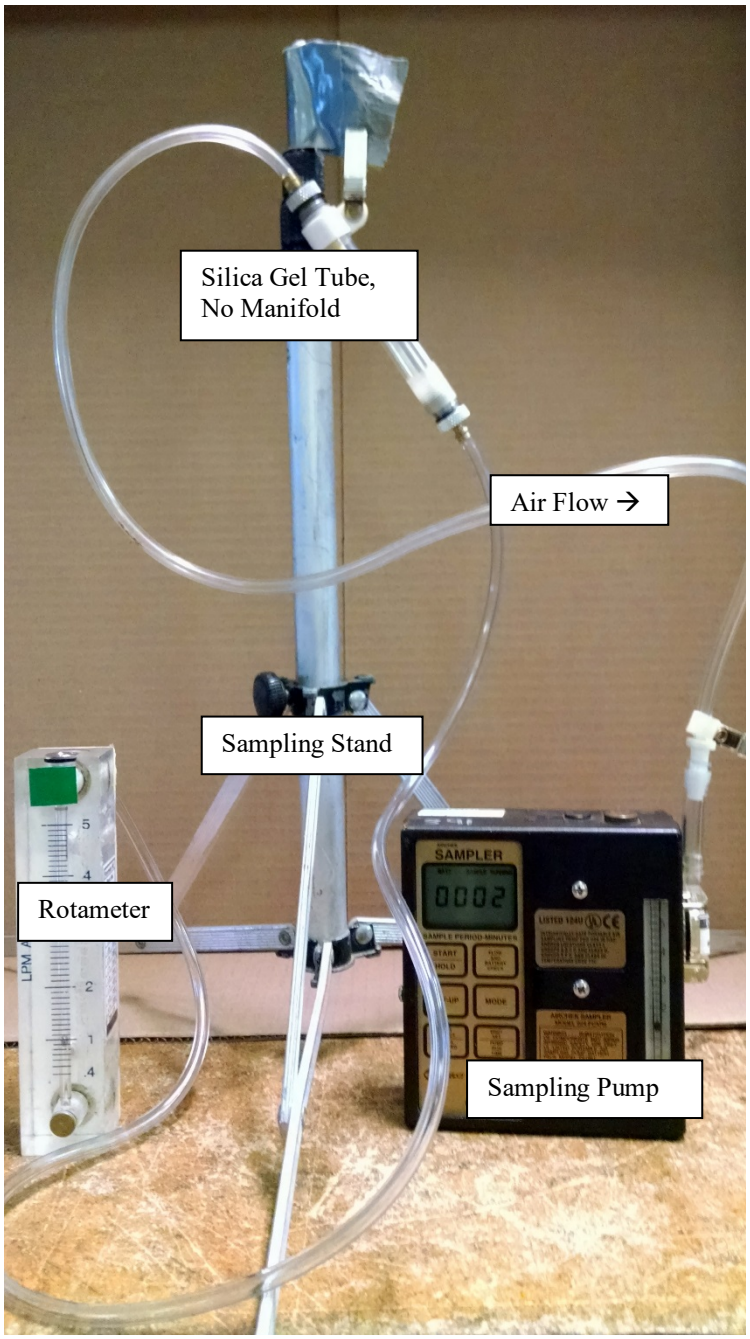


FIGURE 3. Calibration Train (Single Manifold)

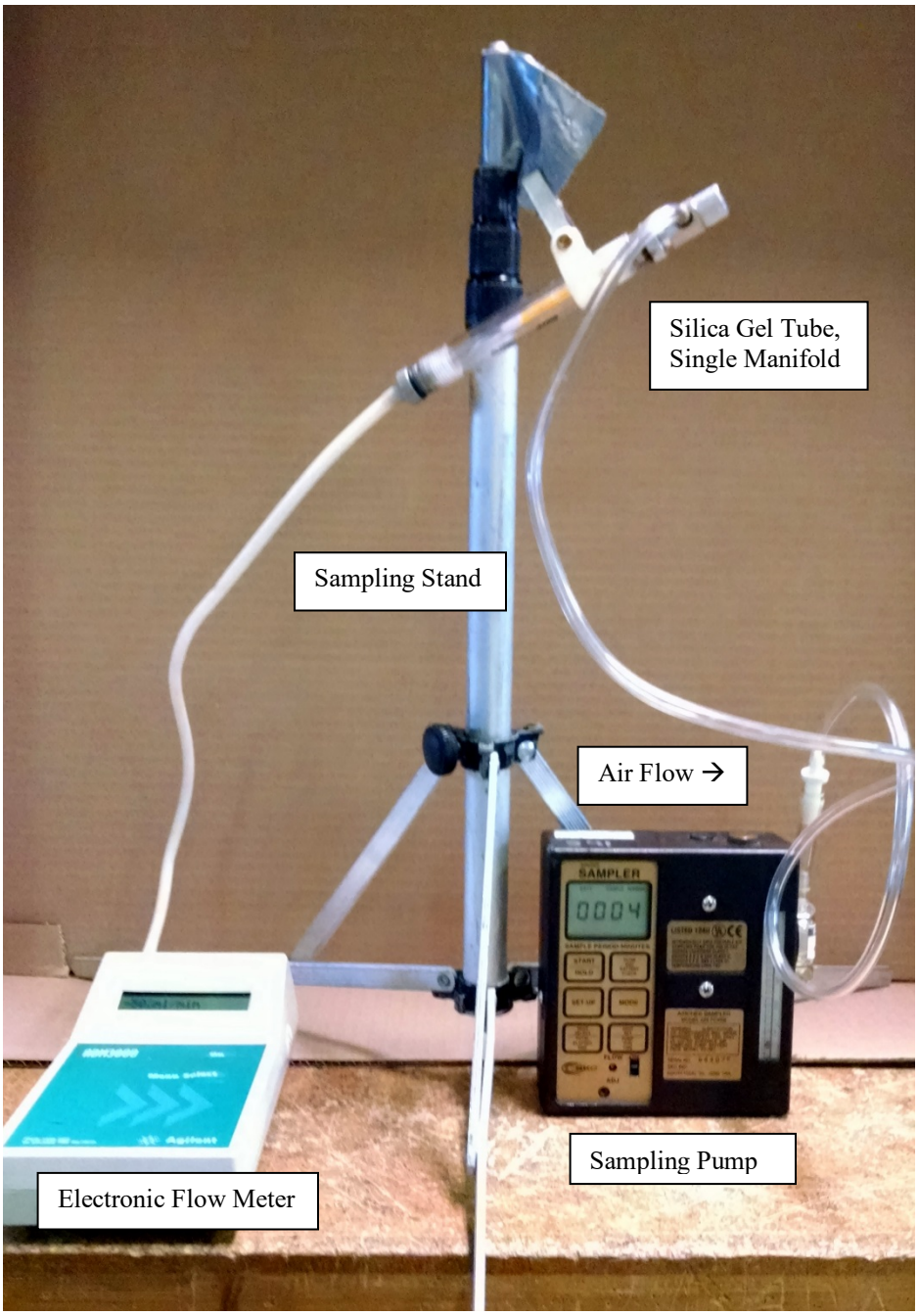


FIGURE 4. Rotameter Calibration Sticker

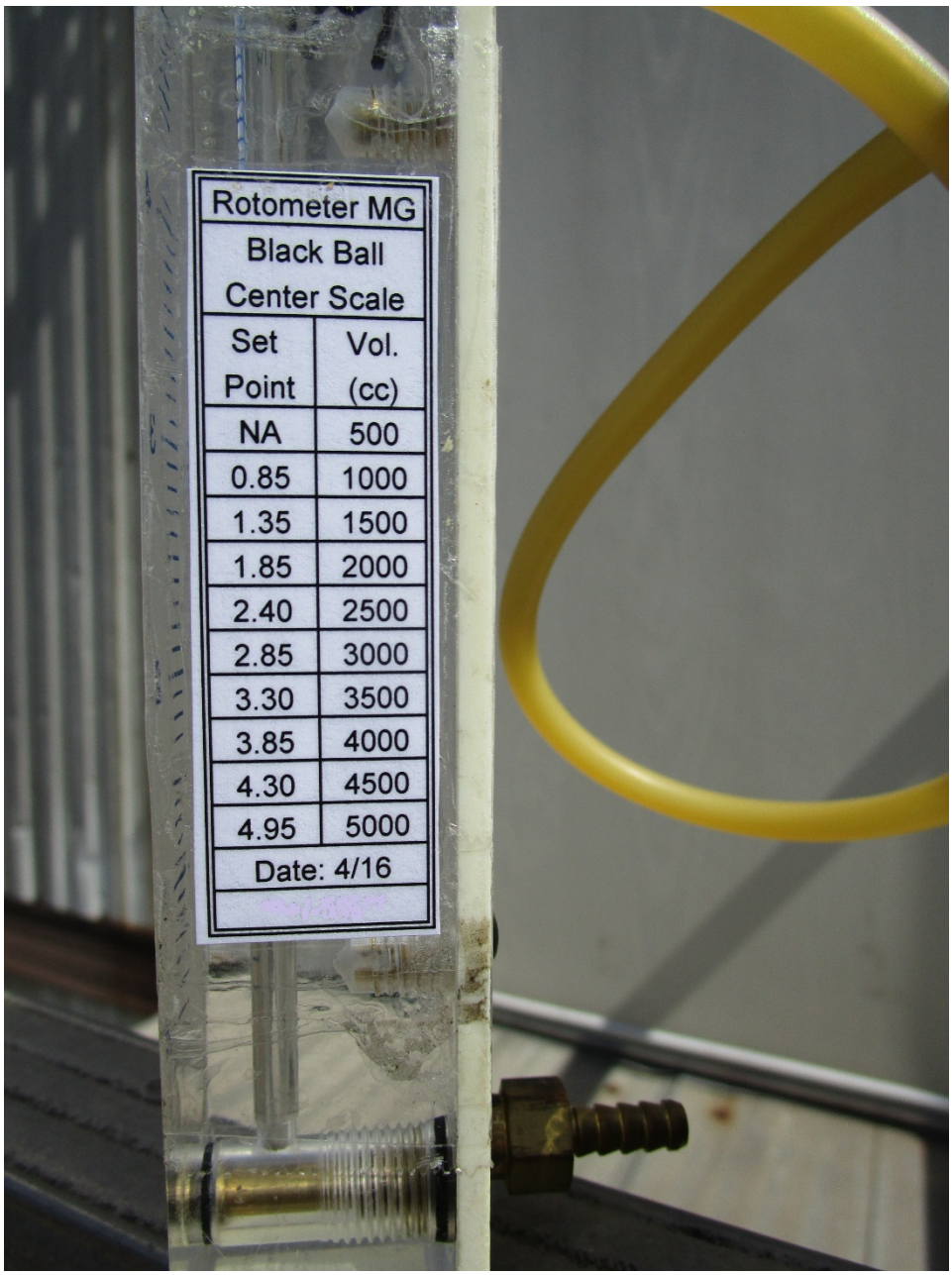


FIGURE 5. Silica Gel Tube Sampling Train (Single Manifold)

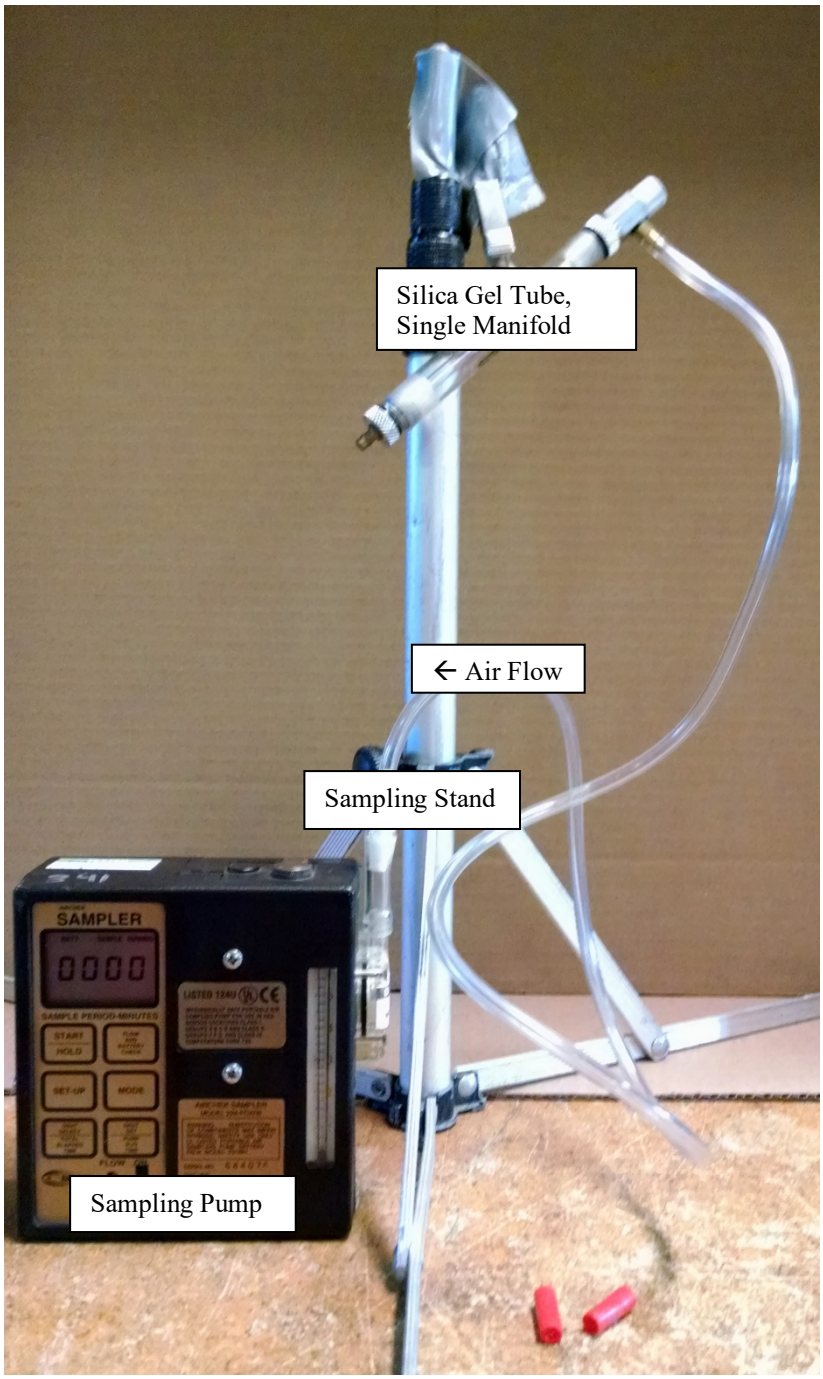


FIGURE 6. Silica Gel Tube Sampling Train (No Manifold)

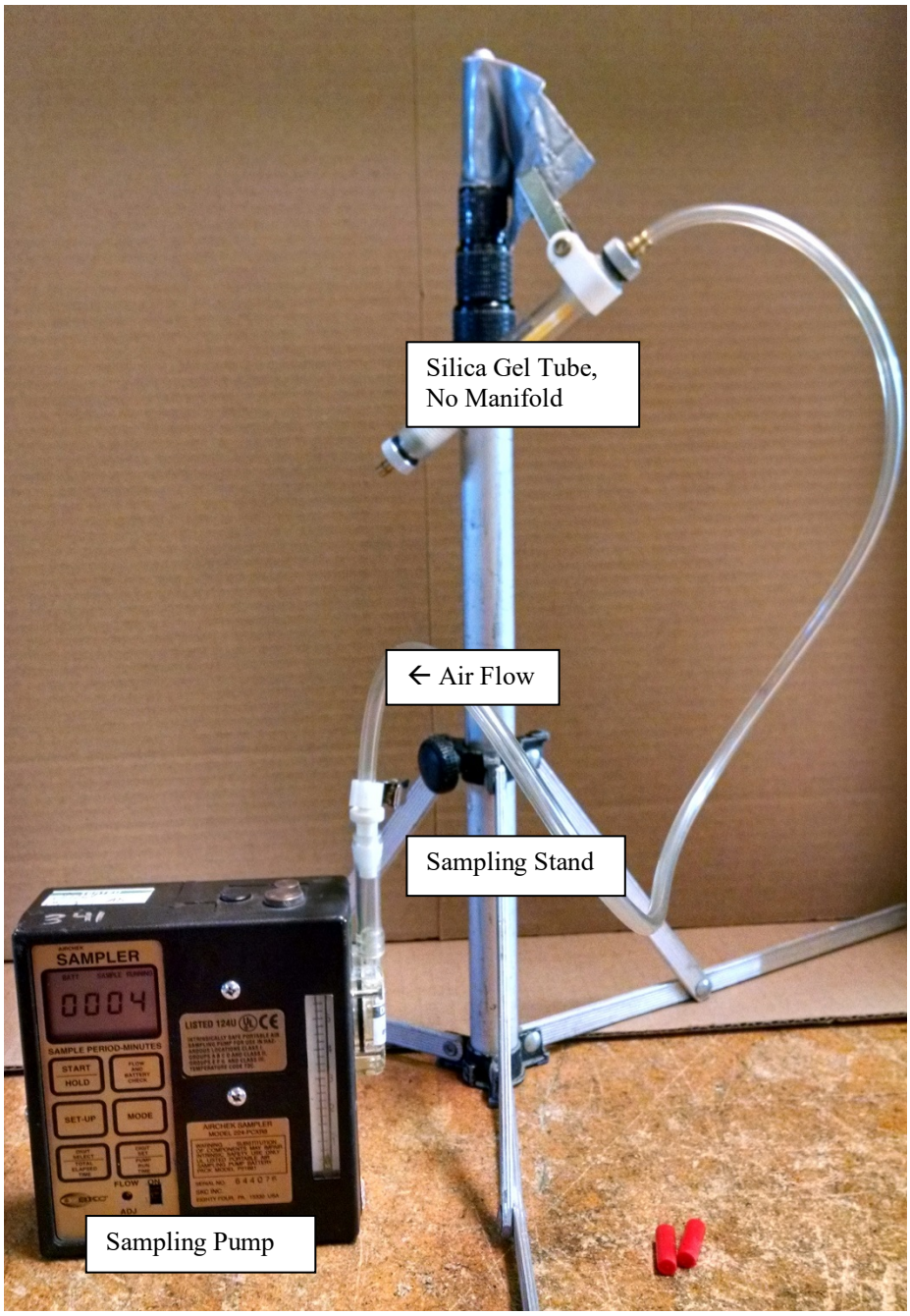
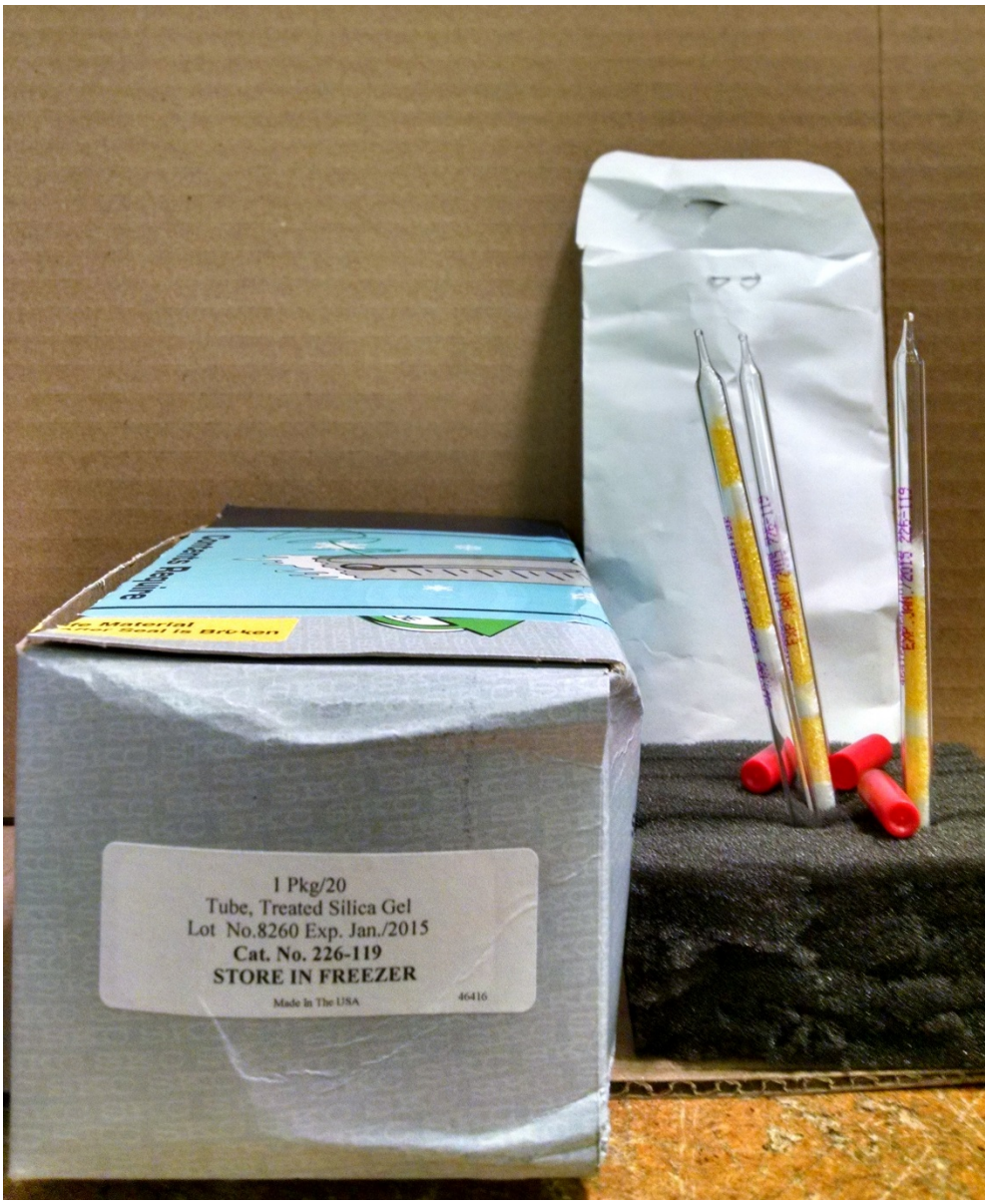


FIGURE 7. Media



APPENDIX C
Air Sampling Worksheet
SOP: ERT-PROC-2131-20
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Air Sampling Worksheet

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EPA/Environmental Response Team
Scientific Engineering Response and Analytical Services Contract
Air Sampling Work Sheet
Leidos Innovations Corporation, Edison, NJ
U.S. EPA Contract No. EP-W-09-031

Site: _____ WA#: _____

Sampler: _____ U.S. EPA/ERTC WAM: _____

Date: _____ SERAS Task Leader: _____

Sample #					
Location					
Pump #					
Media					
Analysis/Method					
Rotameter					
Time/Counter (Start)					
Time/Counter (Stop)					
Total Time					
Pump Fault	Y / N	Y / N	Y / N	Y / N	Y / N
Flow Rate (Start)					
Flow Rate (End)					
Flow Rate Average					
Sample Volume					
MET Station on Site?: Y / N					