National Human Exposure Assessment Survey (NHEXAS)

Arizona Study

Quality Systems and Implementation Plan for Human Exposure Assessment

The University of Arizona
Tucson, Arizona 85721

Cooperative Agreement CR 821560

Standard Operating Procedure **SOP-BCO-L-16.0**

Title: Analysis of Passive Formaldehyde Samplers

Source: The University of Arizona

U.S. Environmental Protection Agency
Office of Research and Development
Human Exposure & Atmospheric Sciences Division
Human Exposure Research Branch

Analysis of Passive Formaldehyde Samplers

1.0 Purpose and Applicability

This standard operating procedure (SOP) describes the methodology used by Air Quality Research (Research Triangle Park, NC) for the analysis of the PF-1 passive formaldehyde samplers using a colorimetric method and chromotropic acid.

2.0 Definitions

2.1 Diffusional (passive) sampler: collects contaminant based on the principle of diffusion; no pump is used to collect the sample.

2.2 Color producing reagent: chromotropic acid disodium salt develops a purple color when added to a solution containing formaldehyde that is acidified with concentrated sulfuric acid..

3.0 References

3.1 Procedure is based on Formaldehyde: Method 3500, NIOSH Manual of Analytical Methods, 3rd ed., Vol. 1, US DHHS Publ. 84-100, pp. 3500-1 to 3500-4, Revised May 1989.

3.2 K.L. Gersling and S.M. Rappaport, "A Passive Sampling Device for Determining Formaldehyde in Indoor Air," Environ. Intl. **8**, 153-158 (1982).

3.3 "Analysis of PF-1 Passive Formaldehyde Monitor," Air Quality Research, Research Triangle Park, NC, revised March 25, 1991.

4.0 Discussion

4.1 This method is used to measure the amount of formaldehyde in PF-1 passive samplers. The PF-1 is a diffusional (passive) monitor designed to collect formaldehyde in air. It consists of a glass tube containing a sodium bisulfite-impregnated filter at the bottom. When the cap is removed from the tube, formaldehyde diffuses through it at a constant rate and is chemically trapped by the reaction that occurs on the surface of the filter. The cap is replaced at the end of the sampling period, which is typically 5-7 days.

4.2 Exposed PF-1 monitors are mailed to Air Quality Research (Research Triangle Park, NC) for analysis. For the analysis, water is added directly to the monitors to elute the collected formaldehyde from the filter. Then, chromotropic acid and concentrated sulfuric acid are sequentially added; the monitors are capped and heated in a water bath for 15 minutes. A purple color develops, the absorbance of which is measured spectrophotometrically at 580 nm to determine the amount of formaldehyde collected.

4.3 The average concentration of formaldehyde in the air sampled is calculated from the amount of formaldehyde measured divided by the product of the diffusion rate and the time exposed.

5.0 Responsibilities

5.1 Fixed-location sampling of indoor and outdoor air for formaldehyde will be conducted by University of Arizona personnel as described in SOP UA-F-13.0..

5.2 The Laboratory Director at Battelle or his designee shall be responsible for shipping exposed PF-1 samplers, received from the University of Arizona, to Air Quality Research (Research Triangle Park, NC) for extraction and analysis.

5.3 Any person who amends or alters this procedure is responsible for ensuring that the changes have been properly documented, the SOP changed, reviewed, and reissued.

6.0 Materials and Reagents

6.1 Materials

6.1.1 Spectrophotometer capable of measuring absorbances at 580 nm. (The spectrophotometer is equipped with a micro-flow-through cell. Care is taken to optimize the flow cell vacuum and cycling times for sampling the viscous solutions.)

6.1.2 Centrifuge (International Equipment Co. Model HN-SEE) equipped with an IEC 958 rotor and IEC 398 tube carriers, operated at 2150 rpm for 15 min.

6.1.3 Vortex mixer.

6.1.4 Heated water bath (Precision Model 186) with removable cover, capable of sustaining a temperature of 90-100°C to a depth of at least 6 cm.

6.1.5 Repipette capable of delivering 3.0 ±0.02 mL aliquots of sulfuric acid.

6.1.6 Volumetric pipettes (0.1, 0.5, 1.0, 2.0, 5.0 and 10.0 mL aliquot delivery).

6.1.7 Glass centrifuge tubes (16 x 100 mm disposable glass culture tubes).

6.1.8 Assorted volumetric pipettes and flasks.

6.1.9 Spectrophotometer cells of 1-cm path length (if spectrophotometer is not equipped with a micro-flow-through cell). Disposable polystyrene spectrophotometer cells may also be used.

6.1.10 Vented 16 mm polypropylene caps to fit glass centrifuge tubes.

6.2 Reagents

6.2.1 Chromotropic acid reagent (4,5-Dihydroxynaphthalene-2,7-disulfonic acid disodium salt): chromotropic acid disodium salt (Reagent No. 230, Eastman Kodak Co., Rochester, NY) or chromotropic acid disodium salt dihydrate (Reagent No. J166-3, J.T. Baker, Phillipsburg, NJ).

6.2.2 Sulfuric acid, reagent-grade.

6.2.3 Sodium bisulfite, reagent-grade.

6.2.4 37% Formaldehyde, 10 mL ampoules (Hach Company, Ames, Iowa).

6.2.5 Deionized distilled water, formaldehyde-free.

7.0 Procedure

7.1 Initial Preparations

7.1.1 Cleaning the Glassware

7.1.1.1 Wash all glassware and related items used in the analysis of passive PF-1 samplers in a 1% (v/v) RBS-35 solution.

7.1.1.2 Rinse all glassware thoroughly with tap water followed by 5 rinses with deionized distilled water.

7.1.2 Preparation of Chromotropic Acid Reagent

7.1.2.1 Dissolve 750 mg of chromotropic acid disodium salt or 880 mg of chromotropic acid disodium salt dihydrate in formaldehyde-free water and dilute to 10.0 mL.

7.1.2.2 Stopper and mix well, making sure that the material dissolves completely.

7.1.2.3 Prepare fresh daily.

7.1.3 Preparation of Formaldehyde Primary Standard Solution (40 μg/mL)

7.1.3.1 Dilute the 10-mL solution in the commercial ampoule with formaldehyde-free water to 100 mL in a volumetric flask to give a 400 μg/mL solution. (When the standard calibration curve is prepared, as described in Section 7.1.6, 5 mL of the 400 μg/mL solution is diluted to 50 mL to give a final working standard solution of 40 μg/mL.)

7.1.3.2 Stopper and seal the 100-mL volumetric flask with parafilm, and place in a refrigerator.

7.1.3.3 The 400 μg/mL solution remains fresh for approximately 1 month.

7.1.4 Preparation of Sodium Bisulfite ($NaHSO_3$) Reagent

7.1.4.1 Dissolve 2.25 g of sodium bisulfite in formaldehyde-free water and dilute to 100 mL in a volumetric flask.

7.1.4.2 Cap and label.

7.1.4.3 Prepare fresh daily.

7.1.5 Preparation of Diluting Reagent

7.1.5.1 Mix two volumes of formaldehyde-free water with three volumes of concentrated sulfuric acid in an acid-resistant flask. Use a repipette and work carefully in a fume hood when adding the H_2SO_4 to the flask.

7.1.5.2 Allow the solution to cool for a few minutes and then cover the flask with parafilm.

7.1.5.3 This reagent may be stored indefinitely if properly sealed.

7.1.6 Preparation of Calibration Standards

7.1.6.1 Use one 200 mL, two 100 mL, and five 50 mL volumetric flasks.

7.1.6.2 Pipette the appropriate aliquot of sodium bisulfite reagent (Section 7.1.8) into its labeled volumetric flask using a pipette, as specified in Table 1.

Table 1. Sodium Bisulfite Reagent

Flask Size (mL)	Sodium Bisulfite Reagent (mL)
200	20
100	10
100	10
50	5
50	5
50	5
50	5
50	5

7.1.6.3 This will give solutions upon dilution that are 10% (volume/ volume) with respect to sodium bisulfite.

7.1.6.4 Transfer aliquots of the 40 µg/mL formaldehyde standard solution (from Section 7.1.3) into the flasks prepared in Section 7.1.6.2 as shown in Table 2:

Table 2. Calibration Standards

Flask Size (mL)	Sodium Bisulfite Reagent (mL)	40 µg/mL Formaldehyde Standard Aliquots (mL)	Calibration Standard (µg/mL)
200	20	0.5	0.1
100	10	0.5	0.2
100	10	1.0	0.4
50	5	1.0	0.8
50	5	2.5	2.0
50	5	4.0	3.2
50	5	5.0	4.0
50	5	---	Blank

7.1.6.5 Dilute all 8 flasks to the mark with formaldehyde-free water.

7.1.6.6 Prepare these calibration solutions fresh daily and immediately prior to analyzing a batch of PF-1 monitors.

7.1.6.7 Transfer 2-mL aliquots of each of the standard solutions to test tubes.

7.1.6.8 Add chromotropic acid color reagent to each and develop the color as described below in Section 7.3.3.

7.1.6.9 Zero the spectrophotometer against the blank solution prepared in Section 7.1.6.4. Repeat this step as needed during the analysis. Prepare a fresh blank solution for each batch of monitors from the 50 mL blank solution.

7.1.6.10 Read the absorbance of each calibration solution at 580 nm and record the data.

7.1.6.11 Generate the calibration curve, as described in Section 7.5.1.

7.2 Preparation of PF-1 Monitors for Analysis

7.2.1 Inspect each vial and cap for cracks, poor seals, or any defect. If any defects are observed, they must be noted on the Analysis Data Sheet.

7.2.2 If a tube is cracked, remove the filter from the bottom and place it in a test tube for analysis. If the crack is such that air may have entered the sampler, the sample is voided and marked "NOT ANALYZED" in the Analysis Data Sheet.

7.2.3 Remove the caps from the PF-1 monitors.

7.2.4 Add 2.0 mL of formaldehyde-free water to each tube and allow to stand for 30 minutes. Vortex occasionally at the maximum power level for 5 seconds.

7.3 Analysis

7.3.1 Add chromotropic acid and develop the color as described in Section 7.4.

7.3.2 Decant the color-developed sample solution into a centrifuge tube.

7.3.3 Clearly mark the tube for identification.

7.3.4 Centrifuge the sample for 15 minutes at about 1,100 x g or until a clear supernatant is observed.

7.3.5 Measure the absorbance of each solution at 580 nm. If spectrophotometer cells are used, decant the sample solution from the centrifuge tube into a cell. If the spectrophotometer contains a micro-flow-through cell, a portion of the sample may be removed directly from the supernatant solution in the centrifuge tube.

7.3.6 If the absorbance of the color-developed sample is greater than the absorbance of the 4.0 µg/mL standard, the sample should be diluted using the diluting reagent (see Section 7.1.5).

7.3.6.1 Withdraw a 1.0-mL aliquot of the color-developed sample using either a volumetric pipette or a positive displacement pipettor (air displacement pipettors do not work well because of the viscosity of the acid mixture).

7.3.6.2 Add 4.0 mL of the diluting reagent.

7.3.6.3 Vortex for a few seconds.

7.3.6.4 Read the absorbance again at 580 nm.

7.3.6.5 The new concentration must be multiplied by a factor of five to arrive at the correct value.

7.4 Addition of Chromotropic Acid Color Reagent

7.4.1 Add 0.10 mL of chromotropic acid reagent to each sample or standard solution using a calibrated 0.10-mL micropipette.

7.4.2 Cautiously add 3.0 mL of concentrated H_2SO_4 to each formaldehyde solution using a fixed volume 3.0-mL repipette in a fume hood. (Caution: Heat is evolved.)

7.4.3 Thoroughly mix the resultant solution for a long count of 5, using a vortex mixer. Ensure that the filter in the field samplers is displaced from the

bottom of the tube by the vortexing action. If not, use a clean glass rod to pull the filter away from the bottom of the tube.

7.4.4 Because of the evolution of heat, wear safety glasses and an impervious glove, and hold the vial containing the solution at the top. Point the vial away from the face while vortexing.

7.4.5 Cover the vials with vented caps or aluminum foil.

7.4.6 Place the capped vials in a hot water bath (90-100°C) and at least 6 cm deep for 15 minutes to allow the color to develop (use a timer).

7.4.7 Remove the vials from the water bath and allow them to cool for at least 30 minutes prior to measuring absorbances.

7.5 Calculations

7.5.1 Calibration Curve

7.5.1.1 Using the calibration standards data (from Section 7.1.6), perform a least-squares linear regression analysis, using a standard personal computer program and an equation of the form $A = a + bF$, where

A = absorbance (in absorbance units, AU)
F = formaldehyde amount (μg)
a = intercept (AU), and
b = slope (AU/μg).

7.5.1.2 Although somewhat dependent on the specific spectrophotometer used, values obtained should be similar to:
slope = 0.250 AU/μg
intercept = 0.001 AU, and
correlation coefficient (R^2) should be greater than 0.999.

7.5.2 Calculation of Formaldehyde Content of PF-1 Samplers

7.5.2.1 Calculate the amount of formaldehyde collected by the exposed PF-1 monitor from the following relationship:

$$F_{exp} = \frac{2\left(A_{exp} - a\right)}{b} \text{ (µg)}$$

where F_{exp} = amount of formaldehyde collected (µg); and A_{exp} = absorbance of the sample at 580 nm.

7.5.2.2 Calculate the amount of formaldehyde present in the blank (unexposed) samplers, using the same relationship.

7.5.2.3 The blank-corrected formaldehyde content of the exposed sampler is given by:

$$F'_{exp} = F_{exp} - F_b \text{ (µg)}$$

where F'_{exp} = blank-corrected formaldehyde content of the exposed sampler (µg); and F_b = formaldehyde content of the blank sampler (µg) (This value is typically ~0.4 µg).

7.5.3 Calculation of Formaldehyde Concentration

7.5.3.1 Calculate the concentration of formaldehyde in the air sampled from:

$$C = \frac{F'_{exp}}{Kt} \text{ x 1000 (ppmv)}$$

where C = concentration of formaldehyde in air sampled (ppmv); t = sampling period during which the monitor was exposed (h); and K = sampling rate for the PF-1 monitor (µg/ppm-hr).

7.5.3.2 The empirically derived sampling (uptake) rate at which formaldehyde is collected on the PF-1 samplers is 0.310 µg/(ppm-hr).

7.5.3.3 To calculate the concentration in mg/m^3 at 25 °C and 760 mm Hg, use the value in parts per million (ppm) determined in Step 7.5.3.1 in the following equation:

$$C(\text{mg} / \text{m}^3) = C(\text{ppmv}) \text{ x } \frac{30.03}{24.45}$$

7.5.3.4 If the sampling temperature and pressure are significantly different from 25°C and 1 atm, respectively, the concentration of formaldehyde is corrected as follows:

$$C_0(\text{mg} / \text{m}^3) = C\frac{101.3\,T}{298\,P}$$

where T = temperature recorded at the sample site (in °K); P = pressure at the sample site (in kPa).

7.6 Quality Control

7.6.1 Spikes, Blanks, and Duplicates

7.6.1.1 The overall performance of the monitoring method is evaluated using spiked controls, blanks, and duplicates.

7.6.1.2 Given the small amounts of material that are collected with the PF-1 tubes, it is important that samplers used as spikes, blanks, duplicates, and field samplers come from the same lot number, since the background compounds present on unexposed samplers may vary significantly from lot to lot.

7.6.1.3 At least one sampler should be prepared for analysis as a field spike, one sampler each presented for analysis as a field blank and an unexposed blank, and one field duplicate sampler taken with every 30 field samples.

7.6.2 Precision, Bias, and Tolerance

7.6.2.1 The coefficient of variation (standard deviation divided by the mean expressed as a percentage) of the method is estimated by Air Quality Research to be 15%.

7.6.2.2 The PF-1 monitor/bubbler bias, defined as the ratio of the mass of formaldehyde uptake of the monitors compared to the uptake by gas sampling bubblers, is reported by Air Quality Research to be 1.01.

7.6.2.3 The tolerance, which is the statistical expectation of deviation in reported monitor results versus the "true" formaldehyde concentration sampled, is specified by Air Quality Research as -25% for the low limit and +25% for the high limit.

7.6.3 Limit of Detection

The limit of detection is estimated by Air Quality Research to be 0.01 ppmv ±15%.

7.6.4 Storage Stability

7.6.4.1 The established shelf life of the PF-1 monitors prior to exposure is 6 months.

7.6.4.2 The established shelf life of the PF-1 monitors after exposure is 1 month.

7.6.5 Corrective Actions

7.6.5.1 The spectrophotometer is re-zeroed after recording the absorbance of the blank reagent solution.

7.6.5.2 If the absorbance of the blank reagent exceeds 0.005 AU, the absorbances of additional blank samples are measured. If all these absorbances exceed 0.005, then stop the analysis and reclean the spectrophotometer before continuing. Check for any problems in the sampling system (e.g., tubing).

7.6.5.3 If the absorbance of the standard solutions differs from those measured when developing the calibration curve by more than 5% or 0.005 AU (whichever is larger), then new standards must be prepared and a new calibration curve developed.

7.6.5.4 Any questionable samples will be rerun.

8.0 Records

8.1 Information about the PF-1 monitors received from UA shall be entered onto the Analysis Request Form, which is submitted along with the monitors to Air

Quality Research for analysis. Figure 1 shows the Analysis Request Form used to submit exposed monitors to Air Quality Research for analysis.

8.2 Analysis results received from Air Quality Research shall be recorded together for each set in a spreadsheet.

8.3 Associated calibration curve and control data shall also be recorded in the spreadsheet.

8.4 Hard copies of the data shall be stored in the data logbook and shall be sent to UA after one-over-one review of the data.

8.5 All forms and logbooks shall also include the technician's signature, date, time of analysis, and method number.

8.6 All completed data forms and results will be submitted to the Laboratory Director where they will be checked and stored in a designated area.

8.7 All forms will be filled out in black ink. Any deletions or corrections shall be made by drawing a line through the error and shall be initialed by the technician making the correction.