California Environmental Protection Agency

Air Resources Board

Method 430

Determination of Formaldehyde and Acetaldehyde in Emissions from Stationary Sources

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STATIONARY SOURCE TEST METHOD
ARB Method 430
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in Emissions from Stationary Sources

1 APPLICABILITY AND PRINCIPLE

Before participating in the conduct of an actual test, test method personnel must read this test method in its entirety and must be trained and experienced by simulation of this test method or by observation of actual testing.

Figures are presented at the end of this document and organized as:

FIGURE 1: TEST METHOD - FLOWCHART;
FIGURE 2: SAMPLING - FLOWCHART;
FIGURE 3: (A-D) ANALYSIS; and
FIGURE 4: (A-C) RECORDING AND REPORTING.

Mention of trade names or specific products related to this test method does not constitute endorsement by the California Air Resources Board. In all cases, equivalent items from other manufacturers or suppliers may be used.

1.1 Applicability

This method applies to the determination of formaldehyde and acetaldehyde emissions from stationary sources. The method is based on the use of high performance liquid chromatography (HPLC).

Any modification of this method shall be subject to approval by the Executive Officer. The term Executive Officer as used in this document shall mean the Executive Officer of the Air Resources Board or Executive Officer (Air Pollution Control Officer) of the Air Pollution Control District/Air Quality Management District in whose jurisdiction the test is conducted, or his or her authorized representative.

Warning: This method has not been validated for exhaust gas streams with high particulate or moisture loading. Special consideration must be given to the interpretation of data from such streams. Unless the tester and data interpreters can account for the possible biases due to such conditions on a source specific basis in advance of actual testing, this method shall not be used on such sources for regulatory purposes. In general, it may be used on a developmental basis. This method failed to produce valid data in exhaust gas downstream from a caustic (NaOH) scrubber at 40% (v/v) H_2O. In this case, the deleterious effects of a basic effluent on the acidic sampling medium may have added to the problems caused by high moisture and grain loading.

NOTE: In this method, any use of the term "aldehyde" shall apply to formaldehyde and acetaldehyde, unless otherwise specified.

1.2 Principle

Gaseous emissions are drawn through a Teflon sample line and two impingers in series, each impinger containing an aqueous acidic solution of 2,4-dinitrophenyl-hydrazine (DNPH). The sample line is rinsed with another aliquot of the same solution. An aldehyde reacts with DNPH by nucleophilic addition on the carbonyl followed by 1,2-elimination of water and the formation of a 2,4-dinitrophenylhydrazone. Acid is required to promote protonation of the carbonyl because DNPH is a weak nucleophile.

After organic solvent extraction, the sample is analyzed using reverse phase HPLC with an ultraviolet (UV) absorption detector operated at 360 nm. Impingers are analyzed separately.

Formaldehyde and acetaldehyde in the sample are identified and quantified by comparison of retention times and area counts of sample extracts with those of standards.

2 SENSITIVITY, RANGE, AND PRECISION

NOTE: The analytical values given below are characteristic of results obtainable by experienced chemists who follow the procedures of this method. The total test method values given below are strongly dependent on sampling and source matrix conditions and are more anecdotal than typical.

2.1 Sensitivity

Analytical Values:

The lowest calibration standard used during the Air Resources Board's development of this method was 0.1 μg/mL.

Total Test Method Values:

The data user must specify the required sensitivity for the entire test method (Target Aldehyde Concentration(s), Section 3.1) before a test as part of the pre-test protocol.

2.2 Range

Analytical Values:

The highest calibration standard used during the Air Resources Board's development of this method was 20.0 μg/mL.

Total Test Method Values:

The range may be extended by dilution.

2.3 Precision

Analytical Values:

The relative standard deviation of multiple lab spike (spike concentration typically 1 μg/mL) recoveries during the Air Resources Board's development of this method was ± 5%.

Total Test Method Values:

Data users who desire an estimate of the test precision must require that the tester use two co-located sampling trains for each sampling run. This will provide three pairs of matched sample data from which precision can be estimated.

EPA conducted quadruplicate testing using a similar test method for formaldehyde at one facility which produces formaldehyde and at another facility which only uses formaldehyde. Producer exhaust concentrations ranged from 0 to 800 mg/m³ and user exhaust concentrations ranged from 0 to 2 mg/m³. Twelve quadruplicate sampling trains were run at each facility with precision estimates (95% prediction intervals) of +3% to +65% with most values clustered in the range of +10% to +40%. There did not appear to be any one precision value that characterized either facility.

3 THE DATA USER AND THE PRE-TEST PROTOCOL

The Data User

If a determination of aldehyde emissions from a stationary source is required as part of a regulatory process, the regulating agency shall be considered the data user or shall designate the data user for the purposes of this method. Otherwise, the data user shall be assumed to be the source owner or operator. In any case, the pre-test protocol must identify the data user.

The data user must choose the target aldehyde concentration(s) and approve the pre-test protocol before testing may begin. Further requirements regarding the target aldehyde concentration(s) are stated in Section 3.1.

The Pre-Test Protocol

A pre-test protocol must be written which documents the test performance criteria of the data user and the calculations of the tester. The protocol must demonstrate that the test performance criteria chosen by the tester will meet the needs of the data user. Additionally, the pre-test protocol shall include all of the other information on supplies, logistics, personnel, etc. necessary for efficient and coordinated test performance.

Warning: Before field sampling per Section 8, the tester and laboratory must demonstrate and document the aldehyde contamination level of at least four reagent blanks (Section 10.2.1.1) which have been flushed through the same length of sample line (Section 5.1.2) and the same sort of impinger (Section 5.1.3) as will be used in the field. These reagent blanks shall be taken just after the preparation of the DNPH impinger solution as described in Section 7.2, Step 4. This information is necessary for the calculations in this section and for the completion of the required pre-test protocol. The laboratory and tester may optionally use a reagent blank concentration based on laboratory records from previous impinger solution preparations. However, if this approach is taken, the option (presented in Section 4.2) of complying with either Section 4.2.1 or 4.2.2 is eliminated and the tester must comply with the requirements of Section 4.2.2 to demonstrate successful performance at a test. (See warning in Section 4.2.)

NOTE: Throughout this section, example calculations are given. References are given to some calculations which are explained more fully in Section 11. Some of the example calculations are based on the performance of this test method on an idling diesel engine which was emitting formaldehyde and acetaldehyde in the ppm range. While these calculations may be used as a first approximation basis for test planning, special consideration must be given to different source test conditions which may substantially alter the results on any other source test.

3.1 Target Aldehyde Concentration(s)

Generally, the regulatory limit established by the Executive Officer (Section 1.1) shall determine the target aldehyde concentration(s) (TAC) for stationary source emissions. If a source test is conducted for regulatory purposes and no regulatory limit has been established, the TAC shall be 1 ppm (1.25 mg HCHO/dscm, 1.83 mg CH_3CHO/dscm).

3.2 Planned Sampling Runs

At least three sampling runs must be performed in series; the average of the results of these sampling runs is defined, for the purposes of this method, as representative of emissions from a stationary source. A fourth run is recommended (optional) to be used for the required matrix spike, since the spiking procedure will increase the limit of detection by a factor of two. It shall be the responsibility of the tester to: (a) access potential variability in emissions with different periods of source operation, (b) secure the cooperation of the stationary source operating personnel, (c) plan sampling runs which will be characteristic of emissions from the stationary source, and (d) document the extent to which the planned sampling runs are representative of emissions from the stationary source.

3.3 Planned Sample Volume

The planned sample volume (PSV) is based on the TAC and the estimated sampling train field blank (ESTFB), and the average percent recovery (R); the PSV shall be calculated using the following formula:

$$\text{PSV (liters)} = \frac{\text{ESTFB (ng) x 10 (AMR)}}{1000} \text{ x } \frac{100}{\overline{R}\ (\%)} \text{ x } \frac{1}{\text{TAC (mg/dscm)}}$$

where:

ESTFB(ng), the estimated sampling train field blank, shall be calculated according to Section 11.3 using pre-test reagent blank analyses as required in Section 7.2.

AMR, the target aldehyde mass ratio (the total sample aldehyde mass (ng) divided by the ESTFB) shall be 10 to 1.

$\overline{R}$ (%), the average percent recovery, shall be calculated according to Section11.5 and shall be based on at least four laboratory spikes as required in Section 10.3.

At standard conditions (20°C and 760 mmHg), TAC conversion factors are:

1 ppm HCHO = 1.25 mg/dscm
1 ppm CH_3CHO = 1.83 mg/dscm

3.4 Planned Sampling Time

Planned sampling time (PST) and appropriate sampling rate should be chosen to yield the sample volume estimated in Section 3.3 without exceeding the absorbing capacity of the impinger solution. The range of the recommended sampling time is determined as follows:

$$\text{PST (minutes)} = \frac{\text{PSV (L)}}{(0.5\ \text{L / min})} \text{ To } \frac{\text{PSV (L)}}{(0.1\ \text{L / min})}$$

3.5 Example Calculations

3.5.1 Planned Sample Volume (PSV)

Assume:

TAC = 1 ppm
= 1.25 mg HCHO/dscm
= 1.83 mg CH_3CHO/dscm

$\overline{C}_{RB}$ = 13.3 ng HCHO/mL (average concentration of at least four reagent blanks of impinger solution per Section 7.2)
= 26.7 ng CH_3CHO/mL
V_{ST} = 24 mL (total impinger solution used per sample train)
$\overline{R}$ = 90% (average recovery of at least four laboratory spikes)

Calculate:

$$ESTFB = 1.5 \times \overline{C}_{RB} \times V_{ST}$$
= 480 ng HCHO
= 960 ng CH_3CHO

$$PSV_{HCHO} = \frac{10 \times 480}{1000} \times \frac{100}{90} \times \frac{1}{1.25}$$
= 4.3 liters

$$PSV_{CH_3CHO} = \frac{10 \times 960}{1000} \times \frac{100}{90} \times \frac{1}{1.83}$$
= 5.8 liters

WARNING: This calculation shows that the planned sample volume may differ for different aldehydes. In this case, it was due to field blanks whose masses are not in the same ratio as the corresponding molecular weights. The larger volume shall be used in such cases.

3.5.2 Planned Sampling Time (PST)

PST = (5.8/0.5) to (5.8/0.1) (3.2)
= 12 to 58 minutes

NOTE: In general, it is better to sample for a longer time at a lower flow rate, when all flow rates yield reasonable PST, as in this case.

4 INTERFERENCES

4.1 Positive Reagent Blanks

Formaldehyde and acetaldehyde contamination during the performance of this test method using the DNPH reagent tend to result in reagent blank concentrations which are greater than the analytical limit of detection determined by a multipoint calibration curve. Because of this, the limit of detection of this method is defined as the upper bound of the 95% confidence interval for the analysts of at least four reagent blanks (Sections 11.2 and 11.6).

4.2 Sampling Interferences

In addition to blanks yielding positive sampling bias, other contaminants can combine with target aldehydes or DNPH to yield negative biases. Two approaches to reducing the deleterious effects of such interferences on data quality are given below, the tester is required to comply with at least one of these two approaches and document such compliance according to Sections 12 and 13.

Source specific matrix interferences can prevent the achievement of reportable results in ways outside the control of the tester. Therefore, by definition, a tester shall be considered to have successfully performed this test method if the requirements of either Section 4.2.1 or 4.2.2 are met.

WARNING: Compliance with the performance criterion of Section 4.2.2 cannot be determined until after all of the costs of testing have been incurred. Testers shall not depend upon meeting this criterion as an alternative to making every practically feasible effort to achieve the requirements of Section 4.2.1.

4.2.1 Hold Time Performance Criteria

No more than two (2) days after the reagent blanks have been taken from the DNPH impinger solution in Section 7.2, Step 4, the procedures for sampling and sample recovery in Section 8.1 and 8.2 shall be completed or new blanks must be taken and analyzed to continue use of that batch of impinger solution.

Within nine (9) days after reagent blanks have been taken from the DNPH impinger solution according to Section 7.2, Step 4, the procedures for sample extraction in Section 8.3 shall be completed; or new field samples (and new reagent blanks) must be taken.

Within thirty-nine (39) days after reagent blanks have been taken from the DNPH impinger solution according to Section 7.2, Step 4, the procedures for sample analysis in Section 8.4 shall be completed; or new field samples (and new reagent blanks) must be taken.

4.2.2 Sample/Blank Ratio Performance Criteria

The sample/field blank ratio for every sampling run shall be equal to or greater than five (5), calculated according to Section 11.9.

4.3 Analytical Interferences

The hydrazone derivatives of formaldehyde and acetaldehyde are easily separated by HPLC from the derivatives of other carbonyl compounds with which DNPH reacts.

5 EQUIPMENT

It is required that all equipment which comes in contact with the sampled gas stream be of stainless steel, glass, Teflon, or other inert materials which do not react with, catalyze reactions of, or absorb the target aldehyde compounds tested by this method. Additionally, the materials must be chosen based on their lack of significant interference with the DNPH complexing reagent used in this test.

WARNING: Use amber glass, aluminum foil, etc. where appropriate to minimize the exposure of all reagents and samples to light.

NOTE: The equipment list in this section is provided as a convenience of those who must procure supplies for this test method, and to summarize and explain aspects of their use. The list may not be exhaustive of every tester's needs, so the entire test method must be read and understood to achieve adequate procurement and avoid costly delays due to supply shortages.

5.1 Sampling Train

A schematic diagram of the sampling train is shown in Figure 2.

5.1.1 Heated Probe

Stainless steel, quartz glass, or other material as appropriate for the stack temperature. The probe is intended to provide mechanical support and protection for the sample line specified below. The probe shall be heated to a temperature above the dew point of the effluent stream, hence, in some cases, it may be heated by the effluent stream. This will prevent condensation and plugging in the sample line. Heated probes which otherwise meet ARB Method 5 specifications are acceptable.

CAUTION: Prolonged exposure of some stainless steels to temperatures above 1400°F may lead to sagging. Quartz glass is better at higher temperatures, but even it may sag at temperatures over 1700°F. Stack-center temperatures, even in steel valid stacks, may melt steel and quartz glass in conditions of flame impingement.

5.1.2 Sample Line

Teflon tubing, 3.2 mm (1/8 inch) outside diameter. Condensation should be minimized by keeping the inside diameter and length of the sample line as small as practically possible; but the sample line should be long enough to reach the center of the stack. Impingers should be kept as close to the stack as practically possible. To reduce the risk of sample contamination, new (unused) tubing shall be used for each sampling train. If the stack temperature is high (greater than 400°F) a quartz sample line may be needed due to the limited thermal range for mechanical stability of Teflon.

5.1.3 Impingers

Small capacity impingers (approx. 35 mL) with grease free gas-tight seals and connections. The bottom part of each impinger may be used as an extraction vial which must be removed after sampling and capped with a gas-tight, non-contaminating cap before transport. Otherwise, careful transfer of impinger contents to extraction vials in a clean room is necessary. Each sampling impinger set must use at least two impingers in series with 10 mL of liquid in each impinger.

5.1.4 Fittings

Leak tight fittings to connect Teflon tubing to the impingers and optional high temperature quartz sample line, if used. (See Figure 1, Impinger Fitting Detail):

Delrin Flangeless Nut and Tefzel Ferrule

Upchurch Scientific, Inc. (Phone: 1-800-426-0191)
619 West Oak Street
POB 1529
Oak Harbor, WA 98277

Capplugs

Protective Closures Company
2250 Elmwood Avenue
Buffalo, NY 14207

NOTE: This is not an endorsement of these products nor a requirement for their use. This description is provided so that at least one equipment configuration is available to testers which has demonstrated adequate performance in actual use. The configuration in Figure 1, using a cut 1/4 inch i.d. Capplug, uses 1/4 inch o.d. glass tubing for the impinger stem. Some impingers do have 1/4 inch o.d stems and will not require modification for this configuration.

5.1.5 Needle Valve

At base of rotameter, a needle valve is used to adjust sample flow rate.

5.1.6 On-Off Valve

An on-off valve should be used downstream from the silica gel cartridge and upstream from the vacuum pump inlet to prevent pressure surges in the sampling system.

5.1.7 Vacuum Pumps

Vacuum pumps shall have sufficient capacity to draw 100 to 500 mL/min against the sampling system back pressure. Battery powered pumps are not recommended.

5.1.8 Sampling System

The vacuum pump console or any other portion of an ARB Method 5 sampling system which meets the requirements of Section 5.1 may be used to reduce duplication of effort and equipment.

5.1.9 Rotameter

Capable of measuring flows from 100 to 500 mL. The rotameter shall be calibrated by a bubble meter before and after sampling. The design shall be for pressure lifting the indicator mass from below, not for suction lifting it from above. The design shall have a needle valve for fine flow control below the indicator mass.

5.1.10 Ice Bath

Wet ice must be used to cool the impingers during sampling.

5.1.11 Transport Container(s)

The purpose of each container is to transport the impinger/extraction vials to and from the sampling site and protect them from breakage and contamination by aldehydes. Depending upon the number of impinger/extraction vials which will fit into each container, some source tests will need more than one container. Additional containers may be needed for storage of stock reagents. Each container must be unbreakable, air tight, and free of organic compounds in its materials of construction.

5.2 Sample Recovery, Extraction, and Storage

The following items are needed:

5.2.1 Pasteur Pipettes

Pasteur pipettes are well suited to rinsing the small bore Teflon sampling line. Several should be on hand so that dedicated pipettes can be used for each rinsing solution and so that each pipette can be marked for a preset rinse volume.

5.2.2 Extraction Vials

25 mL Teflon lined screw cap.

5.2.3 Conical Vials

25 mL Teflon lined screw cap.

5.3 Analysis

NOTE: The terms “variable” and “gradient” are used only to recommend types of equipment which are best for tuning and adjustment. Fixed wave length and isocratic equipment is acceptable.

The following equipment is needed:

5.3.1 High Performance Liquid Chromatograph

A gradient HPLC system complete with column supplies, mobile phase reservoir, high pressure pumps; high pressure syringes, and all required accessories, including an injection valve or an automatic sampler with an optional 20 μL loop injector; compatible strip chart recorder; a data system is recommended for measuring peak areas and retention times.

5.3.1.1 Column

C-18 reverse phase (RP) column (30 cm x 3.9 mm ID)

5.3.1.2 Detector

Variable wavelength UV detector operating at 360 nm.

5.3.1.3 Pump

Gradient pumping system - constant flow.

5.3.2 Sample Filter Units

Such as Gelman AcroPrep syringeless 0.45 nm PTFE membrane sample filter units.

5.3.3 Filtration and Degassing System

5.3.4 Pipettes

Various sizes, 1 to 10 mL.

5.3.5 Volumetric Flasks

Various sizes.

5.3.6 Graduated Cylinder

1 L for preparing the HPLC mobile phase.

5.3.7 Syringe

100 μL appropriate for HPLC injection.

5.3.8 Flask

1 liter for preparing the HPLC mobile phase.

5.3.9 Bottles

Amber glass, with Teflon-lined screw cap for storing DPNH reagent.

5.3.10 Analytical Balance

0.1 mg sensitivity.

5.3.11 Polyethylene Gloves

Used to handle the treated impingers.

5.4 Nitrogen Purged Detector

To limit aldehyde contamination, one or more nitrogen purged desiccators shall be used as required by this method.

6 REAGENTS

Unless otherwise specified, American Chemical Society (ACS) reagent grade (or equivalent) chemicals shall be used.

NOTE: The reagent list in this section is provided as a convenience for those who must procure supplies for this test method, and to summarize and explain aspects of their use. The list may not be exhaustive of the needs of the tester and laboratory, so the entire test method must be read and understood to achieve adequate procurement and avoid costly delays due to supply shortages.

6.1 Sampling

6.1.1 Reagent Grade Water (Deionized, distilled, charcoal filtered)

6.1.2 Impinger Solution (0.05% DNPH in 2N HC1)

Reagent prepared as described in Section 7.

6.1.3 Silica Gel

Silica gel should be indicating type, 6 to 16 mesh. If previously used, dry at 175°C (350°F) for two hours. New silica gel may be used as received. Alternately, other desiccants (equivalent or better) may be used, subject to approval by the Executive Officer.

6.1.4 Quartz Wool

Cleaned by extracting with a 70/30 (v/v) hexane/methylene chloride mixture. Dry in a 110°C oven, and store in a solvent washed glass jar with Teflon-lined screw cap.

NOTE: This reagent may be used, when necessary, to filter particulate matter in the stack at the tip of the probe. In general, it will not be necessary as the sample recovery and extraction steps will separate aldehydes from particulate matter for analysis.

WARNING: If used, quartz wool must be included in the extraction of the first impinger by adding it to the corresponding transport vial in the field.

6.1.5 Ice

For water bath for cooling the impingers during sampling.

6.1.6 Nitrogen

Compressed gas cylinder - 99.999% purity.

NOTE: A source of nitrogen is needed for each nitrogen purged desiccator.

6.2 Sample Recovery

Impinger solution and reagent water are specified in the procedures for sample recovery.

6.3 Analysis

If reagent blanks are too high to meet the data users criteria, blanks should be performed on all analytical reagents separately to isolate the problem.

6.3.1 Reagent Water

Same as 6.1.1.

6.3.2 DNPH

2,4-Dinitrophenylhydrazine (DNPH) - Kodak, reagent grade, or equivalent. Recrystallize at least twice with UV grade acetonitrile before using in standards.

6.3.3 Acetonitrile

UV grade or equivalent.

6.3.4 Mobile Phase

60% acetonitrile /40% water (v/v).

6.3.5 Hexane

Pesticide quality or equivalent.

6.3.6 Methylene chloride

Pesticide quality or equivalent.

6.3.7 Extraction Solvent

Hexane/methylene chloride, 70/30 (v/v).

6.3.8 Ethanol

95% ethanol, reagent grade.

NOTE: Ethanol is needed for preparation of the hydrazone derivatives of the aldehydes and for cleaning the HPLC column.

6.3.9 Hydrochloric Acid

Reagent grade.

6.3.10 Formaldehyde

Reagent grade, highest concentration available (formalin is 30% formaldehyde).

6.3.11 Acetaldehyde

Reagent grade, highest concentration available.

7 PREPARATION OF REAGENTS

7.1 Purification of 2,4-dinitrophenylhydrazine (DNPH) Crystals

DNPH reagents shall be kept in a nitrogen purged desiccator except when specified steps call for handling reagents outside a desiccator. It is best to use a glove box, if one is available.

CAUTION: This procedure involves large amounts of acetonitrile, which must be handled under a properly ventilated hood. The following effects are attributed to the inhalation of acetonitrile. At 500 ppm in air, brief inhalation has produced nose and throat irritation. At 160 ppm, inhalation for four hours has caused flushing of the face (2-hour delay after exposure) and bronchial tightness (5-hour delay). Heavier exposures have produced systematic effects with symptoms ranging from headache, nausea, lassitude to vomiting, chest or abdominal pain, respiratory depression, extreme weakness, stupor, convulsions and death depending upon concentration and length of exposure period.

7.1 Step 1: Prepare a supersaturated solution of DNPH by boiling excess DNPH in 200 mL of acetonitrile.

Step 2: Remove and transfer the supernatant to a covered beaker and allow gradual cooling to room temperature in a nitrogen purged desiccator.

Step 3: Let covered beaker sit overnight.

Step 4: Decant supernatant and discard it. Rinse crystals three times with an amount of acetonitrile which is approximately three times the apparent total crystal volume.

Step 5: To another clean beaker, transfer crystals from the bottom of the beaker in Step 4. Avoid transfer of the less pure crystals from the wall of the beaker. Add 200 mL of acetonitrile, heat to boiling, and again let crystals grow slowly overnight at room temperature in a nitrogen purged desiccator.

Step 6: Repeat rinsing process as described in Step 4. Allow the third rinse to stay in contact with the crystals for at least 30 minutes at room temperature in a nitrogen purged desiccator.

Step 7: Take an aliquot of the second rinse, dilute 10 times with acetonitrile, acidify with 1 mL of 2N hydrochloric acid per 100 mL of DNPH solution, and analyze by HPLC. An ideal purity level is shown in Figure 3 (C).

Step 8: Continue recrystallization until an acceptable purity level is reached.

Step 9: After recrystallization, purity of the DNPH reagent must be maintained by storing in an air tight amber glass bottle which is kept in a room temperature nitrogen purged desiccator.

7.2 Preparation of DNPH Impinger Solution

This procedure must be performed in an aldehyde free environment or in an atmosphere with a very low background aldehyde concentration. Avoid use of plastic and plasticizers. All glassware must be scrupulously cleaned first by washing with soap and water, then rinsing several times with hot water followed by distilled deionized water. Aldehyde free acetonitrile should be used for the final rinse. Contact of reagents with laboratory air must be minimized. Finally, transport of impingers/extraction vials in the special transport container and storage in a nitrogen purged desiccator should limit contamination and help to reduce blank values.

The time between preparation of the impinger solution and source sampling shall be kept as short as is practically possible, preferably less than 48 hours, but may be extended with documentation that contamination is kept under control (See Section 4.2.1).

NOTE: It is recommended that field blank values be kept below 10% of sample values on a total sampling train basis. If a test team maintains performance at this recommended level, then the time between preparation and sampling may be safely extended.

Step 1: Sonicate 250 mg of solid 2,4-dinitrophenylhydrazine and 90 mL of concentrated HC1 in a 500 mL volumetric flask. After crystals have dissolved, fill the flask to the mark with reagent water.

Step 2: Place the DNPH reagent above in an amber glass bottle with a tapered glass cap. Add approximately 50 mL of a 70/30 (v/v) hexane/methylene chloride mixture to the bottle and shake the capped bottle on a reciprocating shaker for 20 minutes. Watch for and relieve pressure buildup during shaking. Decant as much as possible of the organic layer, and then use a disposable pipette to remove the remainder. Discard the organic layer.

Step 3: Extract the DNPH reagent five more times as described in Step 2. Cap the bottle tightly, seal with teflon tape, and store in a nitrogen purged desiccator. Fewer extraction steps may be employed if it is documented that an acceptable lab blank value is obtained as specified in Step 4.

Step 4: Before the laboratory may supply the tester with impinger solution for use in field sampling, the laboratory must analyze at least four 10 mL reagent blanks of the impinger solution according to the requirements of the pretest protocol described in Section 3. The laboratory shall coordinate with the tester to avoid the potential problems described in the warning at the beginning of Section 3.

It is only necessary to flush 2 mL of the impinger solution through the sample line. All of this volume and the rest of the 10 mL shall then rinse the walls of the impinger used as the blank impinger.

After determining the reagent blank for each aldehyde in units of (ng aldehyde) / (mL impinger solution), the average concentration of these reagent blanks ($\overline{C}_{RB}$) shall be calculated per Section 11.2 and used per Section 3 to calculate the estimated sampling train field blank (ESTFB) using the equation in Section 11.3.

WARNING: If $\overline{C}_{RB}$ yields a value of ESTFB which is not acceptable for the intended sampling application, repeat the extraction or report that laboratory services cannot be provided for the intended application of this method.

WARNING: If the blank level is acceptable for the intended sampling application, protect the impinger solution from contamination by storing it in a nitrogen purged desiccator and minimizing its exposure to air until sampling commences.

7.3 Preparation of Hydrazone Derivatives

All of the steps below shall be followed separately for the preparation of two different hydrazone derivatives: one series of steps for the formaldehyde hydrazone derivative, and a second series of steps for the acetaldehyde hydrazone derivative.

Step 1: To a saturated solution of the recrystallized DNPH in 2N HC1, add excess formaldehyde or acetaldehyde solution.

Step 2: Filter the colored precipitate, wash with 2N HC1 and then was with water and let the precipitate air dry.

Step 3: Recrystallize the derivative with ethanol. Allow crystals to grow overnight.

Step 4: Filter and was crystals with cold (<10°C) ethanol.

Step 5: Air dry crystals.

Step 6: Check the purity of the hydrazone derivative by melting point determination and by HPLC analysis of crystals dissolved in acetonitrile.

7.4 Preparation of Hydrazone Standards

7.4.1 Standard Stock Hydrazone Solutions

Prepare high and low concentration standard stock solutions of the hydrazone derivative by dissolving accurately weighed amounts of derivative crystal in acetonitrile.

A high concentration stock solution of 100 mg/mL of each aldehyde is prepared by dissolving volumetrically, in 100 mL of acetonitrile, 70.0 mg of the solid hydrazone derivative of formaldehyde and 50.0 mg of the solid hydrazone derivative of acetaldehyde.

A low concentration stock solution of 100 ng/mL of each aldehyde is prepared by a 1:1000 dilution, in acetonitrile, of each high concentration stock solution in a volumetric flask.

NOTE: The molecular weights of each aldehyde and its hydrazone, respectively are:

Formaldehyde = 30 and 120, acetaldehyde = 44 and 224.

7.4.2 Calibration Standards for Hydrazone Derivative

Prepare at least five concentration levels. Add accurately measured volumes of the stock solution to volumetric flasks and dilute to volume with acetronitrile. One concentration should be near but below the limit of detection (Section 11.6), while the other concentrations should correspond to the expected range of concentrations in real samples (Section 3), or should define the working range of the detector.

WARNING: As discussed in Section 11.6, the limit of detection for this method is based on the average level of positive bias in the reagent blanks (Section 11.2). If the area counts for any reagent blank are less than the area counts for the lowest calibration standard, then prepare standards of lower concentration until all of the reagent blanks can be quantitated.

7.4.3 Storage of Hydrazone Standards

Store all standard hydrazone solutions in air tight amber glass bottles which are kept in a room temperature desiccator. Because the DNPH crystals are saturated with aldehyde at this point, it is not necessary that the desiccator be nitrogen purged. They should be stable for approximately two months.

8 PROCEDURE

WARNING: Eye protection should be worn for all procedures. The impingers shall be charged and rinsed with volumetric pipettes. All other transfers of contents to or from impingers, transfer vials, or extraction vials should be quantified by weight to the nearest 0.1 gm. The impingers and any vials used (including appropriate labels and caps) should be tare weighed and weighed after use, and a record should be made of these weights on the sampling data record (Figure 4 (A)). This is for the purpose of measuring gain or loss both during sampling

and across all transfer operations. Due to the extreme sensitivity to contamination of the reagents in this method, only weight determinations should be allowed for this purpose; any other methods (such as marking lines on containers or measuring volumes with volumetric cylinders) should be a avoided. Indelible marks may be used if weighing is impractical and vapors from markers are analyzed as having no detectable aldehydes (in which case the references to sample weights below may be ignored).

8.1 Sampling Procedure

8.1.1 Pretest Preparation

Each rotameter must be calibrated with a soap bubble meter.

The tester may measure and record the tare weights of all impingers and vials (including appropriate labels and caps) in advance of test time for convenience.

Record the following parameters on the sampling data record (Figure 4(A)): date, sampling location, time, ambient temperature, barometric pressure (if available), relative humidity (if available), flow rate, rotameter setting, sampling impinger ID, and vacuum pump ID.

8.1.2 Charging the Impingers

WARNING: The impingers shall be charged in a clean room, which, in the testers judgment, is as low in aldehyde background concentration as is practically feasible. (Clothing, carpeting, and construction materials in general can be sources of aldehydes.)

Step 1: Measure and record the tare weight of each impinger (including appropriate labels and caps). Dispense a measured 10 mL volume of the DNPH/HC1 solution into each impinger in each sampling set.

Step 2: For each source tested, three field blanks shall be taken as in Step 1 and recorded. At this point in the procedure, a field blank shall consist of: (a) an impinger which is as similar to a sampling impinger as is practically feasible, and (b) the same length of unused sampling line as is used to take samples. It is only necessary to flush 2 mL of the impinger solution through the sample line. All of this volume and the rest of the 10 mL shall then rinse the walls of the impinger used as the blank impinger. With the sole exception of not drawing sample gas through the field blanks, all of the same procedures performed on the samples from this step through to the end of analysis per this test method shall be performed on the field blanks.

Step 3: Seal each impinger. Keep containers vertical throughout sampling, transport, and analysis to avoid losses.

Step 4: Measure and record the weight of each impinger and its contents.

Step 5: Securely place the impingers in a special container (Section 5.1.11) for transport to the sampling location. Alternatively, if the impingers are charged in a clean room at the sampling site, the impingers may be placed in and transported to the sampling site in the sampling train ice bath and its container.

Step 6: Record the performance of these steps and the ID of each impinger.

WARNING: The clean room may be a laboratory remote from the field site or a clean room at the field site. If it is remote from the field site, special consideration must be given to the risk of leakage of the impinger contents during transport.

NOTE: The tester must check each impinger after transport to establish that there is no loss of contents.

8.1.3 Preparation of Sampling Train

NOTE: Silica gel may be loaded into any leak tight vessel, not necessarily an impinger. It is not a source of sample contamination as it is downstream from the DNPH sampling solution.

Step 1: Before sampling, remove a sampling impinger set from the special container. To reduce contamination, keep all openings of the sampling train sealed until sampling is about to begin.

Step 2: Just before the source is ready to be tested, open the caps on the field blanks and the sampling equipment.

Step 3: Then, using polyethelyne gloves, assemble the sampling train as shown in Figure 2. All personnel shall wear clean polyethylene gloves when involved in sampling procedures.

8.1.4 Leak-Check Procedures

Before sample collection, perform a leak check on the sampling train. No post-test leak check is required to minimize sample contamination.

Step 1: Close the on-off valve, then start the vacuum pump.

Step 2: Seal the inlet end of the sample line with a clean gloved finger.

Step 3: Slowly open the on-off valve, carefully allowing pressure equilibration with the vacuum pump without flushing impinger contents. After pressure equilibration, the rotameter shall not indicate any flow through the sampling equipment. If this criterion is met go to Step 5; otherwise, go to Step 4.

Step 4: Stop the vacuum pump and slowly roll the sealing finger off of the inlet end of the sampling line, carefully allowing pressure equilibration with the atmosphere without flushing impinger contents. Repeat Steps 1 to 3 until successful.

Step 5: Stop the vacuum pump and slowly roll the sealing finger off of the inlet end of the sampling line, carefully allowing pressure equilibration with the atmosphere without flushing impinger contents. This completes the leak check.

WARNING: If a sample is taken without meeting the leak check criterion, the sample shall be marked and reported as suspect.

8.1.5 Sampling Train Operation

Step 1: Adjust the needle valve on the rotameter to a setting which corresponds to the desired sampling rate based on prior calibration.

Step 2: Close the on-off valve, then start the vacuum pump.

Step 3: Slowly open the on-off valve, carefully allowing pressure equilibration with the vacuum pump without flushing impinger contents. After pressure equilibration, fine tune the rotameter needle valve to the desired setting.

Step 4: Operate the sampling train for the desired sampling time; make a record of any variation of any parameters on the sampling data record. The operator must observe the rotameter during the sampling period and adjust the needle valve to ensure a constant flow rate. The operator must measure and record the sampling flow rate at the beginning, at fifteen-minute intervals during the sampling period, and at the end of the sampling period to determine sample volume.

Step 5: At the end of the sampling period, close the on-off valve to terminate sample flow, then stop the vacuum pump. The operator shall follow this sequence and take any other actions necessary to avoid flushing the impinger contents.

Step 6: Complete the record for the sampling period just finished. Make a note of any unusual events during the sampling period.

8.2 Sample Recovery

Inspect the sampling train prior to and during disassembly and note any abnormal conditions. Disconnect the impingers using polyethylene gloves and treat them as follows:

8.2.1 Sample Recovery from Sample Line

NOTE: For the sample line rinse, the first (upstream) impinger may be used as an extraction and transport vial if it can be secured for transport with no leakage of gas or liquid.

Step 1: Using a Pasteur pipette, rinse the sample line using 2 mL of impinger solution into the extraction vial.

Step 2: Using a Pasteur pipette, rinse the sample line with 1 mL of reagent water into the extraction vial.

Step 3: Establish a gas and liquid tight seal on the extraction vial.

Step 4: Measure and record the weight of the extraction vial and its contents.

Step 5: Securely place the extraction vial in a special container for transport to the laboratory.

Step 6: Record the performance of these steps and the extraction vial ID.

8.2.2 Sample Recovery from Impingers

NOTE: The two impingers may be used as transport and extraction vials if they can be secured for transport with no leakage of gas or liquid. In this case, Steps 1 through 4 below may be omitted.

Step 1: For the first (upstream) impinger, carefully decant its contents into the extraction vial which received the sample line rinse.

Step 2: For the second (downstream) impinger, carefully decant its contents into a separate extraction vial.

Step 3: Using a Pasteur pipette, rinse each impinger with 2 mL of impinger solution into its extraction vial.

Step 4: Using a Pasteur pipette, rinse each impinger with 1 mL of reagent water into its extraction vial.

Step 5: Establish a gas and liquid proof seal on each extraction vial.

Step 6: Measure and record the weight of the extraction vial and its contents.

Step 7: Securely place the extraction vial in a special container for transport to the laboratory.

Step 8: Record the performance of these steps and the extraction vial ID.

8.3 Sample Extraction and Storage

WARNING: All samples must be extracted as soon as practically feasible, but within seven days of collection; and all samples must be completely analyzed as soon as practically feasible, but within 30 days of extraction.

WARNING: The laboratory must measure and record the total weight of each extraction vial and its contents after transport to establish that there is no loss of contents. The weight of the contents shall be recorded as the difference of the total weight and the tare weight of the vial. Careful attention to details of sample identification and chain of custody are required for the transfer of samples from field to laboratory personnel.

WARNING: The samples from the sampling impingers must be extracted and analyzed separately. This avoids dilution of low concentration samples and provides information about sampling efficiency. Note that the first impinger contents were combined with the sample line rinse.

8.3.1 Sample Extraction

Step 1: Upon arrival from the field, if any sample volume in any extraction vial is greater than 15 mL, split into another extraction vial until all vials contain 15 mL or less.

Step 2: Record the ID of each extraction vial and the weight of its contents.

Step 3: Add 10 mL of 70/30 (v/v) hexane/methylene chloride to each vial.

Step 4: Shake the sample vials in a horizontal position on a reciprocating shaker for 20 minutes.

Step 5: Allow the organic layer to separate from the water phase. If an emulsion interface between layers is present, the analyst must complete the separation by centrifugation.

Step 6: As each extraction reaches this step, the chemist must carefully combine in the same conical vial any sibling extracts from samples which were split in Step 1 but which actually belong together. Using a clean pipette, remove

and transfer the organic layer to a conical vial which is unambiguously and indelibly labeled to indicate its related field sample. Do not transfer any water to the vial. Dry at room temperature using nitrogen blowdown.

Step 7: Steps 1 through 6 must be performed three times on each sample to ensure complete extraction. After final combination and blowdown, add 1 mL acetonitrile to each conical vial and seal each one.

8.3.2 Sample Storage

Transfer the conical vials (containing completed extracts and labeled with correlated field sample identification) to a nitrogen purged desiccator for storage. All samples must be completely analyzed within 30 days of extraction.

8.4 Analytical Procedure

WARNING: The method is restricted to use by or under the supervision of analysts experienced in the use of high performance liquid chromatography and the interpretation of the resulting chromatogram. The analyst must demonstrate acceptable performance as required in Section 10.

WARNING: The samples from the sampling impingers must be extracted and analyzed separately. This avoids dilution of low concentration samples and provides information about sampling efficiency. Note that the first impinger contents were combined with the sample line rinse.

Step 1: Establish HPLC operating conditions recommended in Section 9. Calibrate the system daily as described in Section 9. Elute (1) methanol, (2) acetonitrile, and (3) mobile phase each for 20 minutes. Before each analysis, check the detector baseline to ensure stable operation.

Step 2: Draw an (approximately) 100 μL aliquot of the sample into a clean HPLC injection syringe and flush the sample loop. Flush the sample loop in the same manner two more times using the third flush to load the sample loop. Inject the sample after the sample injection loop (20 μL) is loaded. The first samples to be analyzed must be blanks followed by calibration standards and quality control samples. Use the same size loop for calibration standards, quality control samples, and unknown samples.

Alternatively, an automated constant volume injection system may also be used. The data system, if used, must be activated simultaneously with the injection, and the point of injection marked on the strip chart recorder.

Step 3: After allowing sufficient operating time to displace all of the sample out of the loop and onto the column, return the injection valve to the "load" position so that the sample loading operation can be repeated.

Step 4: Rinse or flush the syringe and valves with mobile phase in preparation for the next sample analysis.

Step 5: After elution of the hydrazone derivative (Figure 3 (D)), terminate data acquisition and calculate the component concentrations as described in Section 11.

Step 6: Allow the detector baseline to stabilize before analyzing the next sample. After a stable baseline is achieved, the system may be used for further sample analyses as described above. After several sample analyses, any buildup of contaminants on the column may be removed by flushing with several column volumes of 100% acetonitrile.

Step 7: If the concentration of analyte exceeds the linear range of the instrument, dilute the sample with acetonitrile. Carefully measure any dilution and calculate a dilution factor (≤ 1) for use in final calculations. Analyze again.

Step 8: Compare the retention time(s) of the peak(s) in the sample chromatogram with those of the peaks in the standard chromatograms. The width of the retention time window used to make identifications must be based upon measurements of actual retention time variations of standards over the course of a day. If the retention time is not duplicated ($\pm$ 10%), run a new calibration curve.

WARNING: The chromatographic conditions described here have been optimized for the detection of formaldehyde and acetaldehyde in samples taken from combustion exhaust streams. Analysts are advised to experiment with their HPLC system to optimize chromatographic conditions for their particular analytical needs. The entire analysis for any one source test must be run on only one set of conditions.

9 CALIBRATION

Maintain a record of all calibrations.

9.1 Sampling

Each rotameter shall be calibrated before and after each field test. Perform the following steps to calibrate each rotameter:

Step 1: Assemble a sampling train as shown in Figure 1, but with water in the impingers.

Step 2: Perform a leak check.

Step 3: Connect a soap bubble flow meter to the sampling train inlet.

Step 4: Determine the rotameter readings corresponding to 100, 250, and 500 mL/min.

Step 5: Record the results specific to each rotameter ID.

9.2 Analytical

Step 1: Assemble the HPLC system as shown in Figure 3(A). The following operating conditions are recommended as typical:

Column: BondaPak C-18 (3.9 mm i.d. x 30 cm) or equivalent

Mobile Phase: 60% acetonitrile/40% water, isocratic

Detector: Model 500 UV/v is operation at 360 nm

Sample Rate: 1 point/sec

Sensitivity: 1.00 absorbance units full scale (AUFS)

Flow Rate: Typically 1.0 mL/min

Run Time: Typically 25 minutes

Retention Time: Typically 13.5 minutes for formaldehyde

Injection Volume: Typically 20 μL

NOTE: Other columns, chromatographic conditions, or detectors may be used if the requirements of Section 10 are met. The chromatographic conditions described here have been optimized for a gradient HPLC (Varian Model 5000) system equipped with a UV detector, an automatic sampler with a 20 μL loop injector and a BondaPak C-18 (3.9 mm x 3 cm) column, a recorder, and an electronic integrator. Analysts are advised to experiment with their HPLC systems to optimize chromatographic conditions for their particular analytical needs.

Step 2: Prepare the HPLC mobile phase by mixing 600 mL of acetontrile and 400 mL of water. Place a constant back pressure restrictor (350 kPa) or short length (15-30 cm) of 0.25 mm (0.01 inch) I.D. Teflon tubing after the detector to eliminate further mobile phase out gassing.

Step 3: Place the mobile phase in the HPLC solvent reservoir, set the pump at a flow rate of 1.0 mL/minute, and pump for 30-60 minutes before the first analysis. Start the detector at least 30 minutes before the first analysis and display the detector output on a strip chart recorder or similar output device at a sensitivity of 1.00 AUFS. Once a stable baseline has been achieved, the system is ready for calibration.

Step 4: Inject a minimum of five calibration standards using the same technique that will be used to introduce samples into the HPLC. Analyze each calibration standard according to Section 8.4. The retention times of the analyte must agree within 2%. Tabulate peak height or area counts against the mass injected. Use the results to prepare a calibration curve. A linear response range of approximately 0.05 to 10 ng/μL should be achieved for 20 μL injection volumes.

NOTE: The average response factor may be used in place of a calibration curve if linear response has been documented. One or more daily calibration standards may be used to verify the working calibration curve or response factor. For such verification use intermediate concentration standards near the anticipated levels of the analyte but at least ten times the detection limit. Use the response for the daily calibration standard to calculate a response factor (RF) according to Section 11.1. The daily RF for the analyte should not vary from the predicted RF by more than 10%. If greater variability is observed, recalibrate or develop a new calibration curve from fresh standards.

Step 5: Check the calibration of the instrument of each run (20 or fewer samples) by analyzing a laboratory spike (Section 10.2.1.2).

WARNING: All calibration results shall be calculated and reported as nanograms of aldehyde per area count. This avoids confusion about whether results are based on aldehyde or hydrazone mass.

10 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

10.1 Sampling QA/QC

10.1.1 Field Blanks

For each source tested, three impinger and sample line field blanks shall be taken. A field blank shall consist of an impinger and sample line which is as similar to a sampling impinger as is practically feasible. With the sole exception that the field blanks will not have sample gas pulled through them, and the field blanks shall have all of the same procedures performed on them as are performed on the samples from the beginning of Sampling Procedure (Section 8.1) through to the end of Analytical Procedure (Section 8.4).

NOTE: The reporting requirements for this method specify field blank corrected values. The average of the field blank values for analysis of formaldehyde and acetaldehyde is subtracted from each corresponding sample value. Such values must be clearly identified as field blank corrected. In addition, the field blank values must be clearly identified and reported separately.

10.1.2 Matrix Spikes

For each source tested, the contents of the first impinger from one of the three or more serial sample runs shall be split into two equal portions after sample recovery but before extraction. One split shall be spiked with a known quantity of formaldehyde and acetaldehyde. Each known quantity shall be the amount corresponding to the target concentration chosen by the data user to calculate the emissions sample volume based on the volume of the split.

NOTE: The percent recovery of the matrix spike is a reporting requirement of this method. The matrix spike result is required to guide the data user in the interpretation of the test results.

10.2 Analytical

Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the ongoing analysis of laboratory spikes (Section 10.2.1.2) as a continuing check on performance.

The laboratory must maintain permanent performance records to document the quality of data that are generated. The laboratory must compare the results of their ongoing data quality checks with established performance criteria to determine if the analytical results are acceptable.

In recognition of the rapid advances occurring in HPLC, the analyst is permitted options to improve separations. Such modifications are subject to approval by the Executive Officer. The analyst must also produce data to demonstrate that the options do not interfere with adequate detection of the target source concentration chosen by the data user.

10.2.1 Contamination Checks

Before processing any field samples, the analyst must demonstrate, through analysis of a reagent blank and at least four laboratory spikes, that interferences from the analytical system, glassware, and reagents are under control. Each day, and after each set of 20 or more samples is extracted and analyzed, and if there is a change in reagents, a reagent blank and a laboratory spike must be analyzed as a safeguard against chronic laboratory contamination.

10.2.1.1 Reagent Blank

The analyst must run a reagent blank on DNPH impinger solution along with each set of samples (20 or fewer). Reagent blanks shall have all of the same procedures performed on them as are performed on the samples from the beginning of Sample Recovery (Section 8.2) through to the end of Analytical Procedure (Section 8.4). The exposure to air and other sources of contamination for a reagent blank shall be kept to a practical minimum in a manner consistent with good laboratory practice.

10.2.1.2 Laboratory Spikes

On a continuing basis, the laboratory must spike, with standard stock hydrazone solution, at least one 10 mL blank of DNPH impinger solution per analytical batch of 20 or fewer samples to assess the accuracy of the analytical procedure. Laboratory spikes shall have of the same procedures performed on them as are performed on the samples from the beginning of Sample Recovery (Section 8.2) through to the end of Analytical Procedure (Section 8.4). The aldehyde concentrations of the hydrazone spike shall correspond to the target concentration chosen by the data user. Calculate the percent recovery of the spikes according to Section 11.5.

WARNING: When the percent recovery of a laboratory spike is outside the warning limits (Section 10.4.3), the analyst shall iteratively perform new laboratory spikes and until a laboratory spike is within the warning limits. If unsuccessful, the analyst shall recalibrate and run a new laboratory spike iteratively until the laboratory spike is within the warning limits; this is mandatory if any laboratory spike recovery exceeds the control limits. In the case of such recalibration, the analyst must reanalyze all samples back to the time of the previously successful laboratory spike.

10.3 Quality Control (QC) Samples

10.3.1 Before Contracting for Laboratory Services

As an initial demonstration of acceptable performance, the laboratory must document the ability to generate acceptable laboratory accuracy and precision with this method, using at least four quality control (QC) samples. QC samples are recovered, extracted, and analyzed using the same procedures as for field samples.

To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following steps:

Step 1: Prepare at least four 10 mL QC samples by the procedures for laboratory spikes (Section 10.2.1.2).
Step 2: Prepare the QC samples according to the recovery and extraction steps for field samples.

Step 3: Analyze the QC samples.

Step 4: Calculate the average percent recovery ($\overline{R}$) and the standard deviation of the four recoveries according to Section 11.5.

Step 5: Compare $s_{\overline{R}}$ and $\overline{R}$ with the performance criteria provided by the data user for accuracy and precision. If $\overline{R}$ and $s_{\overline{R}}$ meet the performance criteria, the system is acceptable for the purpose of calculating a planned sample volume (PSV) as required by Section 3.3. Otherwise, the analyst must locate and correct the source of the problem and repeat the process beginning with Step 1.

10.3.2 After Contracting for Laboratory Services

Laboratory spikes performed according to Section 10.2.1.2 (which are within the warning limits given in Section 10.4.3) shall be statistically combined with earlier QC sample results to yield a new $\overline{R}$ and $s_{\overline{R}}$ according to Section 11.5.

Even if, by active default, the data user specifies no accuracy or precision criteria, $\overline{R}$ is still required, based on all QC samples and laboratory spikes, for final adjustment of aldehyde mass analyses in Section 11.

10.4 Accuracy and Precision Limits of Analysis

10.4.1 Accuracy

Accuracy is represented by $\overline{R}$ which is the positive or negative bias of recovery, extraction, and analysis.

10.4.2 Precision

Precision of response to replicate HPLC injection must be ± 10 %RSD or less, day to day, for calibration standards. Precision of retention times must be ± 10 %RSD or less, day to day, for calibration standards. Precision of retention times must be ± 2 %RSD on a given day.

NOTE : $\%RSD = (s \div R) \times 100\%$

10.4.3 Warning and Control Limits

Calculate upper and lower control limits for method performance as follows:

$$\text{Upper Warning Limit (UCL)} = \overline{R} + 2s_{\overline{R}}$$
$$\text{Lower Warning Limit (LCL)} = \overline{R} - 2s_{\overline{R}}$$

$$\text{Upper Control Limit (UCL)} = \overline{R} + 3s_{\overline{R}}$$
$$\text{Lower Control Limit (LCL)} = \overline{R} - 3s_{\overline{R}}$$

Where: $\overline{R}$ and $s_{\overline{R}}$ are as calculated using the equations in Section 11.5. The UCL and LCL shall be used to construct control charts which permanently record trends in laboratory performance.

10.5 Standing Operating Procedures (SOPs)

Testers must generate SOPs describing the following activities in their laboratory:

(1) assembly, calibration, and operation of the sampling system with make and model of equipment used;

(2) preparation, purification, storage, and handling of sampling reagent and samples;

(3) assembly, calibration, and operation of the HPLC system with make and model of equipment used; and

(4) all aspects of data recording and processing, including lists of computer hardware and software used.

SOPs must provide specific step wise instruction and should be readily available to and understood by the laboratory personnel conducting the work.

10.6 HPLC System

The general configuration of the HPLC system should be similar to that illustrated in Figure 3 (A).

11 CALCULATIONS

11.1 Response Factor (Analytical Calibration)

NOTE: The response factor may be from a calibration curve or may be an average response factor according to Section 9.2, Step 4.

$$RF = \frac{C_{cal} \times V_{inj}}{A_{cal} \times 1000} \qquad \frac{(\text{ng aldehyde})}{(\text{area counts})}$$

Where:

C_{cal}	=	Calibration concentration	(ng/mL)
V_{inj}	=	Volume injected into HPLC	(μL)
A_{cal}	=	Area counts for C_{cal} and V_{inj}	(area counts)

11.2 Average Concentration of Reagent Blanks

$$\overline{C}_{RB} = \text{Average concentration of at least four reagent blanks}$$

$$= \frac{\sum_{i=1}^{n} (C_{RB_i})}{n} \qquad \text{(ng/mL)}$$

Where:

n = The number of reagent blanks

C_{RB_i} = Concentration of "i^{th}" reagent blank

$$= RF \times \frac{A_s}{DF} \times \frac{V_{ext}}{V_{inj}} \times \frac{1}{V_{RB_i}} \qquad \text{(ng / mL)}$$

Where:

NOTE: The concentration is not recovery corrected.

A_s	=	Area counts for sample injection	(area counts)
DF	=	Dilution factor (≤1) from Section 8.4	(ratio)
V_{ext}	=	Final extract volume	(mL)
V_{inj}	=	Volume injected into HPLC	(mL)
V_{RB_i}	=	Volume of "i^{th}" reagent blank	(10.00mL)

11.3 Estimated Sampling Train Field Blank

$$ESTFB = 1.5 \times \overline{C}_{RB} \times V_{ST}$$

Where:

$\overline{C}_{RB}$	=	Average Concentration of at least for reagent blanks (impinger solution)	(ng/mL)
V_{ST}	=	Estimated volume of all impinger contents and rinses in a typical sampling train	(mL)

11.4 Concentration of QC Sample (Laboratory Spike)

$$C_{QCS(LS)} = RF \times \frac{A_s}{DF} \times \frac{V_{ext}}{V_{inj}} \times \frac{1}{10.00} \quad \text{(ng/mL)}$$

Where:

NOTE: The concentration is not recovery corrected.

As	=	Area counts for sample injection	(area counts)
DF	=	Dilution factor (≤1) from Section 8.4	(ratio)
V_{ext}	=	Final extract volume	(mL)
V_{inj}	=	Volume injected into HPLC	(mL)
10.00	=	Volume of QC Sample (Laboratory Spike)	(mL)

11.5 Average, Standard Deviation, and %RSD of Percent Recovery

$\overline{R}$ = Average percent recovery of at least four QC samples (laboratory spikes)

$$= \sum_{i-1}^{n} \left(R_i\right) \quad (\%)$$

Where:

R_i = Percent recovery of the "i^{th}" QC sample (laboratory spike)

$$= \frac{C_{QCS(LS)} - \overline{C}_{RB}}{(\text{Known Concentration})\,(ng/mL)} \times 100\% \quad (\%)$$

$\overline{C}_{RB}$ = Average reagent blank concentration (ng/mL)

i = The "i^{th}" QC sample (laboratory spike)

n = The number of QC samples (laboratory spike)

$s_{\overline{R}}$ = Standard deviationof percent recovery (%)

$$= \left(s_{\overline{R}}^{2}\right)^{0.5}$$

Where:

$$s_{\overline{R}}^{2} = \frac{1}{n - 1} \times \sum_{i=1}^{n} \left(R_i - \overline{R}\right)^2 \quad (\%^2)$$

$\%RSD_{\overline{R}}$ = Relative standard deviation of percent recovery

$$= \frac{s_{\overline{R}}}{\overline{R}} \times 100\% \quad (\%)$$

11.6 Limit of Detection

The limit of detection is the upper bound of the 95% confidence interval for the reagent blank.

$$C_{LOD} = \overline{C}_{RB} + \left(\frac{t}{n_{RB}^{0.5}} \times s_{RB}\right) \quad (ng/mL)$$

Where:

$\overline{C}_{RB}$ = Average reagent blank concentration

t = The two - tailed 95% "t" statistic at (n - 1) degrees of freedom where "n" is the number of reagent blanks used to calculate $\overline{C}_{RB}$

$n_{RB}^{0.5}$ = The square root of n

s_{RB} = The satandard deviationof the reagent blanks

11.7 Concentration of a Field Sample

$$C_{FS_i} = \frac{\sum m_{ald}}{V_{ST_i}} \quad (ng/mL)$$

Where:

V_{ST_i} = Volume of all impinger contents (mL)

$\sum m_{ald}$ = Summation of the mass of an aldehyde in all components of a sample train (ng)

Where:

m_{ald} = Mass of an aldehyde in any component

$$= \frac{RF}{(\overline{R}/100)} \times \frac{A_s}{DF} \times \frac{V_{ext}}{V_{inj}} \quad \text{(ng)}$$

11.8 Average Concentration of Field Blanks

$\overline{C}_{FB}$ = Average Concentration of at least three impinger field blanks

$$= \frac{\sum_{i=1}^{n} C_{FB_i}}{n} \quad \text{(ng)}$$

Where:

n = The number of field blanks

C_{FB_i} = Concentration of "i[th]" field blank

$$= \frac{RF}{\overline{R}/100\%} \times \frac{A_s}{DF} \times \frac{V_{ext}}{V_{inj}} \times \frac{1}{V_{FB_i}} \quad \text{(ng/mL)}$$

V_{FB_i} = Volume of "i[th]" recovered field blank ($\geq$ 10 mL)

11.9 Sample/Blank Ratio

$$Ratio_{S/B_i} = \frac{C_{FS_i}}{\overline{C}_{FB}} \quad \text{(ratio)}$$

Where:

$Ratio_{S/B_i}$ = Sample/Blank ratio of "i[th]" sample (ratio)

C_{FS_i} = Concentration of "i[th]" field sample (ng/mL)

$\overline{C}_{FB}$ = Average concentration of field blanks (ng/mL)

WARNING: If the sample to field blank ratio is less than five, then the reporting limit shall be used rather than C_{BCFS_i} (Section 11.10) in all further emissions calculations:

Reporting Limit (RL) = $5 \times \overline{C}_{FB}$

11.10 Concentration of Blank Corrected Field Samples

C_{BCFS_i} = Concentration of "i[th]" blank corrected field sample

$$= \left(C_{FS_i} - \overline{C}_{FB}\right) \quad \text{(ng/mL)}$$

Where:

C_{FS_i}	=	Concentration of "i[th]" field sample	(ng/mL)
$\overline{C}_{FB}$	=	Average concentration of field blanks	(ng/mL)

11.11 Volume of Sample of Source Emissions

$$V_{s_i} = \frac{\left(t_{stop} - t_{start} \times Q_s\right)}{10^6} \quad \text{(dcm)}$$

Where:

V_{s_i}	=	Volume of "i[th]" sample of source emissions	(dcm)
t_{stop}	=	Time at the of sampling	(minutes)
t_{start}	=	Time at the beginning of sampling	(minutes)
Q_s	=	Sampling flow rate	(mL/min)

11.12 Standard Volume of Sample of Source Emissions

$$V_{s(std)_i} = V_{s_i} \times \frac{293}{273 + T_m} \times \frac{P_{bar}}{760} \quad \text{(dscm)}$$

Where:

$V_{s(std_i)}$	=	Standard volume of "i[th]" sample of source emissions	(dscm)
293	=	Standard temperature (20° C)	(°K)
273	=	Conversion (0° C)	(°K)
T_m	=	Rotameter temperature	(°C)
P_{bar}	=	Barometric pressure during test	(mmHg)
760	=	Standard pressure (1atm)	(mmHg)

11.13 Mass Concentration of Aldehyde in Source Emissions

Warning: If the sample to field blank ratio is less than five, then the reporting limit (RL)

(Section 11.9) shall be used rather than C_{BCFS_i} (Section 11.10) in all further emissions calculations.

$$C_{m_i} = \frac{C_{BCFS_i} \times V_{ST_i}}{V_{s(std)_i}} \div 10^6 \quad \text{(ng/dscm)}$$

Where:

C_{m_i}	=	Mass concentration of aldehyde in source emissions for "i^{th} sample	(mg/dscm)
C_{BCFS_i}	=	Concentration of "i^{th}" blank corrected field sample	(ng/mL)
V_{ST_i}	=	Volume of sample recovered from "i^{th}" sample train	
$V_{s(std)_i}$	=	Standard volume of source emission for "i^{th}" sample	(ratio)
10^6	=	ng/mg	

11.14 Volume Concentration of Aldehyde in Source Emissions

$$C_{V_i} = C_{m_i} \times \frac{24.05}{MW_{ald}} \quad \text{(ppm}_V\text{)}$$

Where:

C_{V_i}	=	Volume concentration of aldehyde in source emissions for "i^{th}" sample	(ppm$_V$)
24.05	=	Standard molar volume at 20° C at 1 atm	(L/gmol)
MW_{ald}	=	Molecular weight of aldehyde: use 30 for formaldehyde use 44 for acetaldehyde	(g/gmol)

11.15 Average, Standard Deviation, and Relative Standard Deviation of Source Emission Concentrations

$$\overline{C} = \text{Average aldehyde mass concentration for } \geq 3\ C_i$$

$$= \sum_{i=1}^{n} C_i \quad \text{(appropriate concentration units)}$$

$$s_{\overline{C}} = \text{Standard deviation of average concentration}$$

$$= \left(s_{\overline{C}}^{\,2}\right)^{0.5} \quad \text{(appropriate concentration units)}$$

Where:

$$s_{\overline{C}}^{\,2} = \frac{1}{n-1} \times \sum_{i=1}^{n} \left(C_i - \overline{C}\right)^2 \quad \text{(appropriate units)}^2$$

$$\%RSD_{\overline{C}} = \text{Relative standard deviation of average concentration}$$

$$= \frac{s_{\overline{C}}}{\overline{C}} \times 100\% \quad (\%)$$

12 DATA RECORDING

Figures 4 (A-C) are examples of forms for recording sampling run data and chain of custody records for samples and their coordinating log. Information contained in these forms must be used during performance of test procedures and a permanent record of them must be kept by the tester and laboratory for each test performed.

The tester and laboratory must make and keep any additional records which are necessary for documenting the basis for any reported results. In particular, a narrative description of procedures performed according to the responsibilities detailed in Figure 1 must be written by the tester and laboratory for those procedures for which each is responsible.

13 REPORTING REQUIREMENTS

The data user shall receive a result of "less than reporting limit" (<RL) for any sampling run which has a sample/blank ratio which is less than five (Section 11.9). The reporting limit is five times the average field blank concentration. Such a result can be a part of a successful performance of this test method. See Section 4.2 for important details.

At a minimum, any report to a tester from a laboratory must include the results of all laboratory calculations described in Section 11.

At a minimum, any report to a data user from a tester must include the results of all calculations described in Section 11.

A full report of data recorded according to Section 12 and reported per this section must be maintained by the tester for at least three years. For all tests required or requested by the local Air Pollution Control/Air Quality Management District, ARB, U.S. Environmental Protection Agency or other government agency, these records shall be made available to the Executive Officer upon request.

14 ALTERNATIVE TEST METHODS FOR FORMALDEHYDE AND ACETALDEHYDE

Alternative test methods may be used provided that they are equivalent to Method 430 and approved in writing by the Executive Officer of the Air Resources Board. The ARB Executive Officer may require the submittal of test data or other information to demonstrate equivalency.

15 REFERENCES

(1) "Formaldehyde: A Candidate Toxic Air Contaminant," ARB/SS-88-02. March 1988.

(2) Method T05. "Method for the Determination of Aldehydes and Ketones in Ambient Air Using High Performance Liquid Chromatography (HPLC)," in *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, EPA-600/4-84-041. April 1984.

(3) Method T011. "Method for the Determination of Formaldehyde in Ambient Air Using Absorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC)," in *Compendium of Methods for the Determination of Toxic Organic compounds in Ambient Air*, EPA-600/4-84-041. December 1986.

(4) Southern Research Institute. "Development of Analytical Methods for Ambient Monitoring and Source Testing for Toxic Organic Compounds," Volume I. Literature Review. Project 5614. California Air Resources Board. October 31, 1986.

(5) Southern Research Institute. "Development of Analytical Methods for Ambient Monitoring and Source Testing for Toxic Organic Compounds," Volume II. Experimental Studies. Project 5614. California Air Resources Board. October 31, 1986.

(6) "Development and Validation of a Test Method for Formaldehyde Emissions," EPA Contracts No. 68-02-4125 and 68-02-4550. Jimmy C Pau, Contract Officer. September 1989.

FIGURE 1

TEST METHOD - FLOW CHART

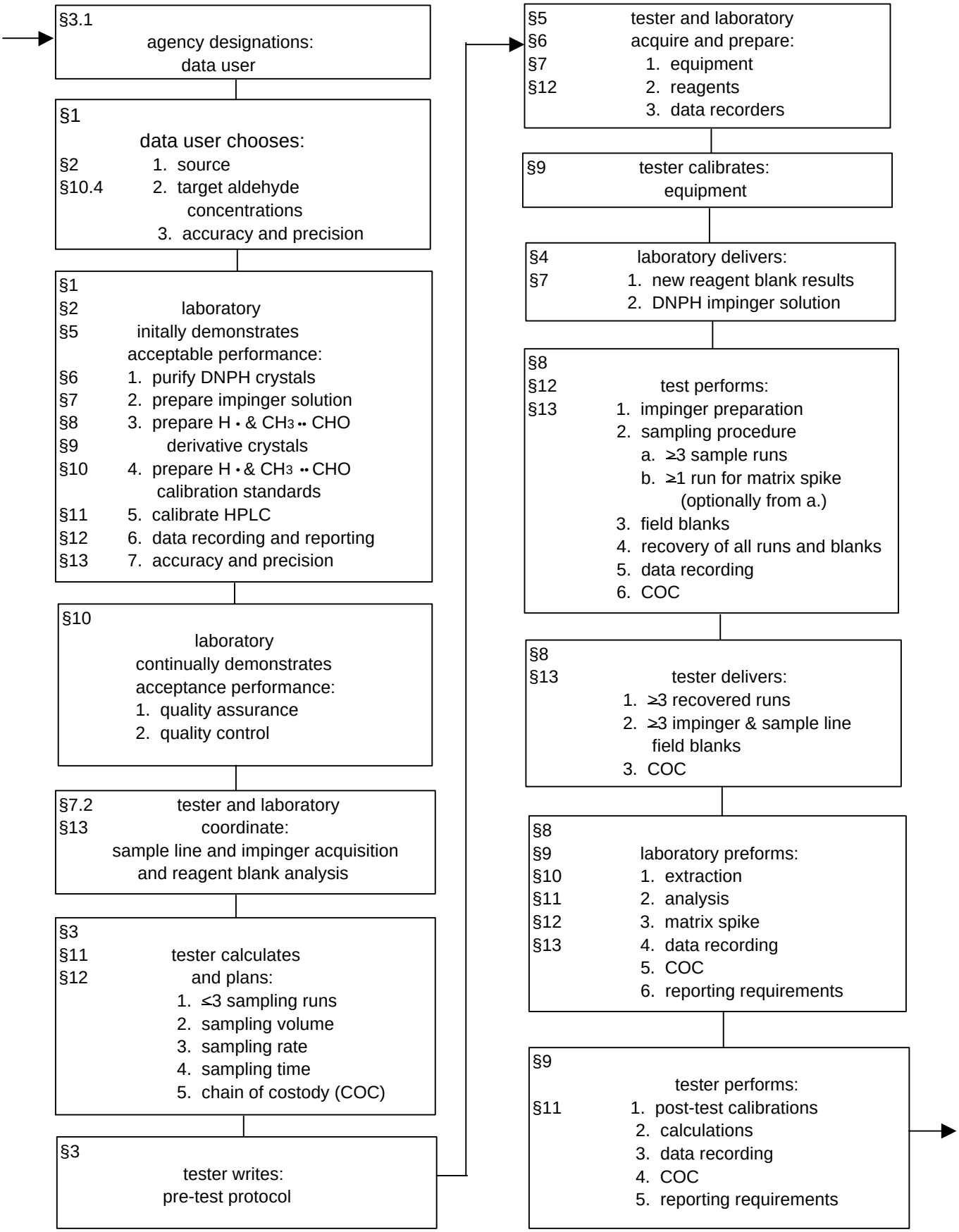

Figure 2

SAMPLING - FLOW CHART

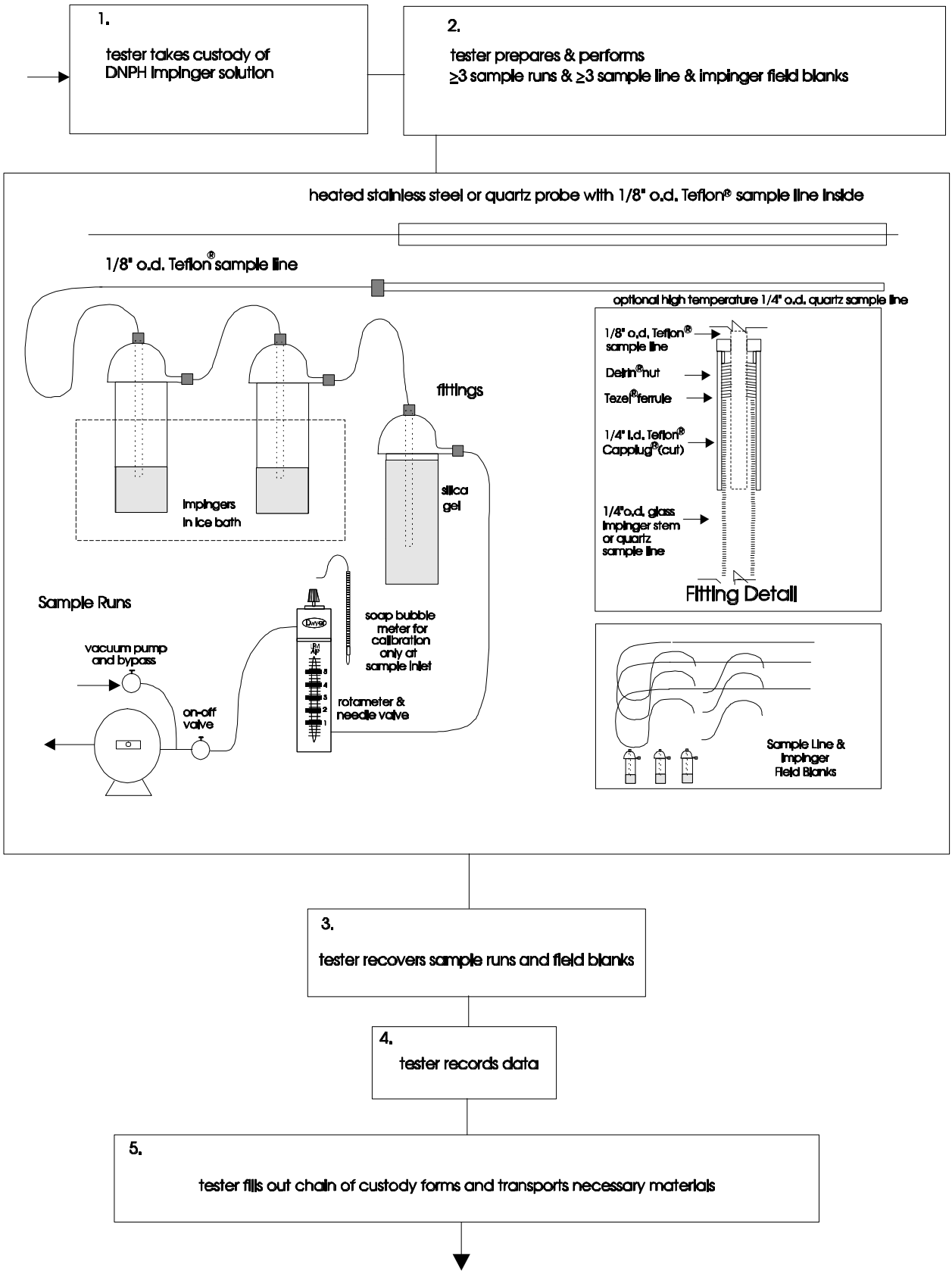

FIGURE 3 (A)

ANALYSIS - TYPICAL HPLC SYSTEM (ref. 2)

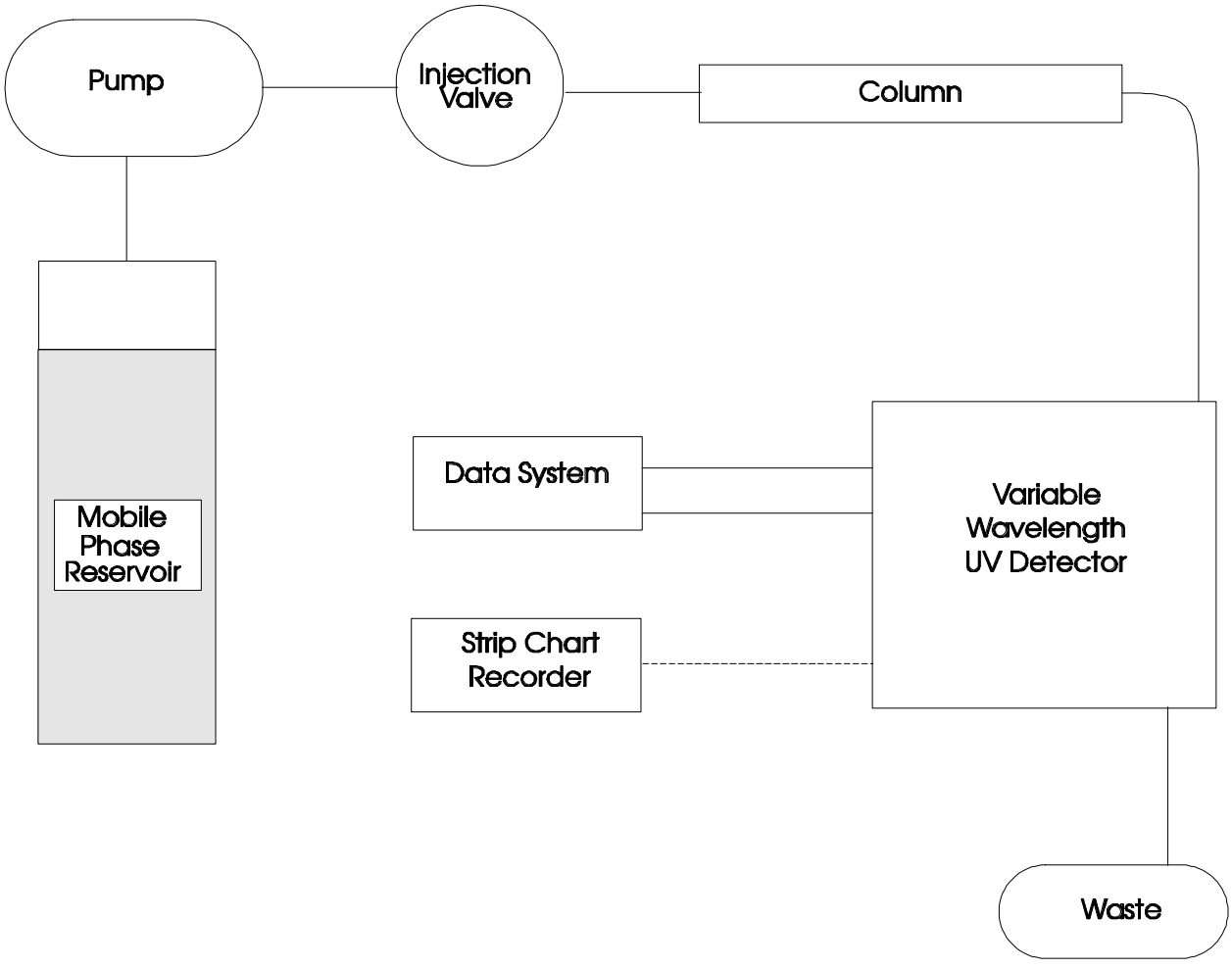

Figure 3 (B)

ANALYSIS - TYPICAL HPLC CHROMATOGRAM (Ref 2)

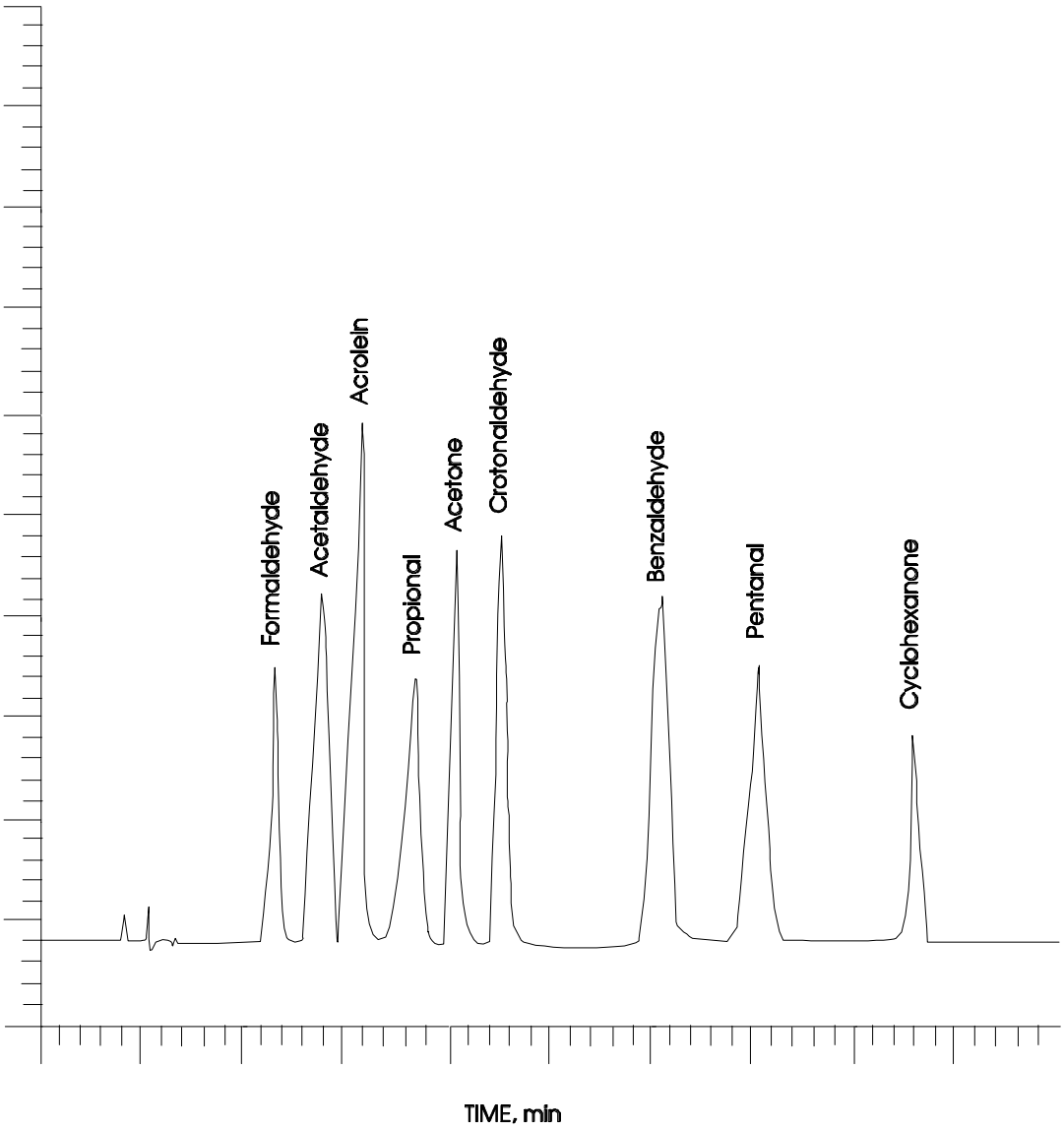

FIGURE 3: (C)

ANALYSIS - TYPICAL PURITY LEVEL OF DNPH AFTER RECRYSTALLIZATION (Ref. 3)

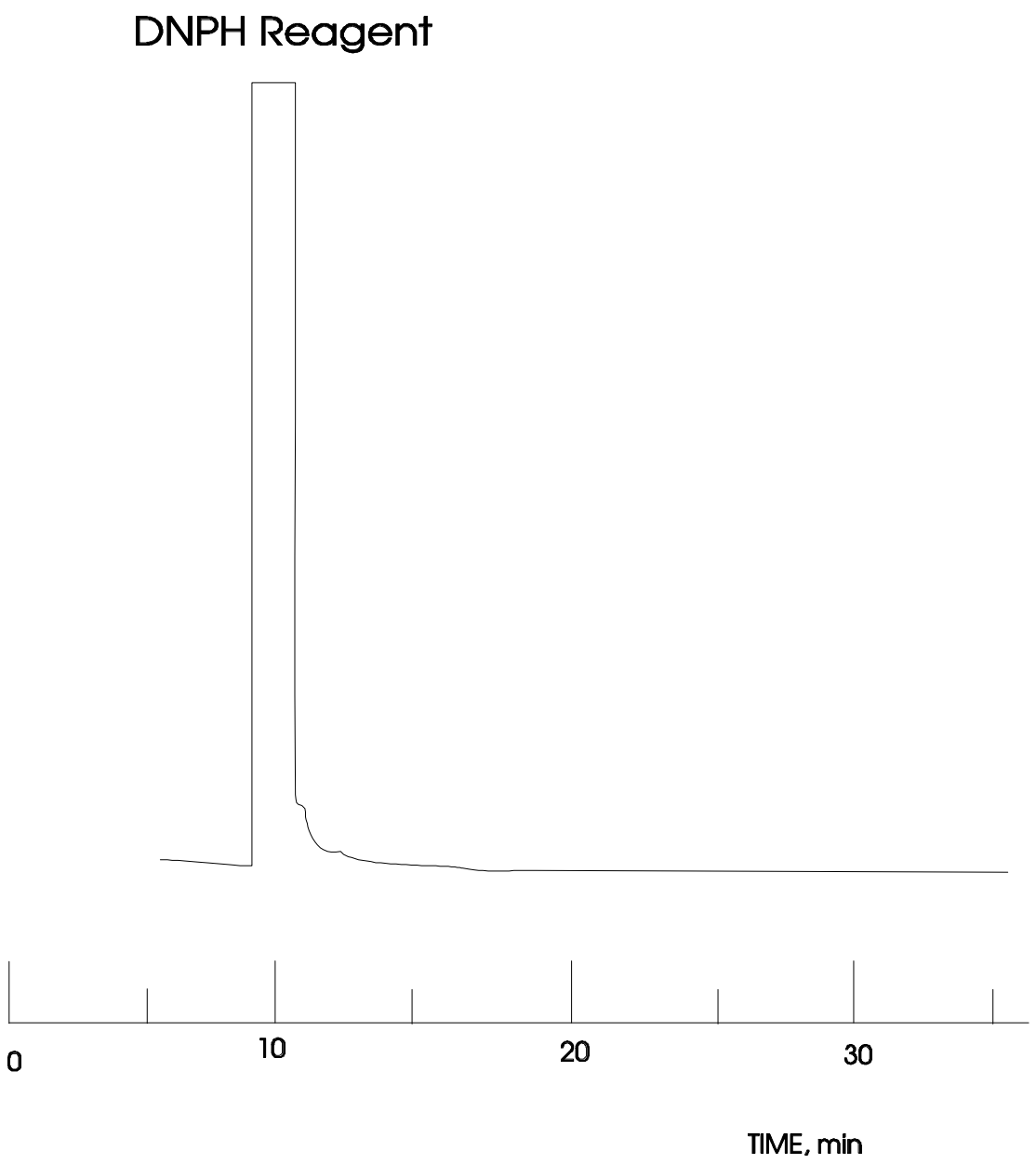

FIGURE 3: (D)

ANALYSIS - TYPICAL CHROMATOGRAPH OF HYDRAZONE DERIVATIVE (Ref 3)

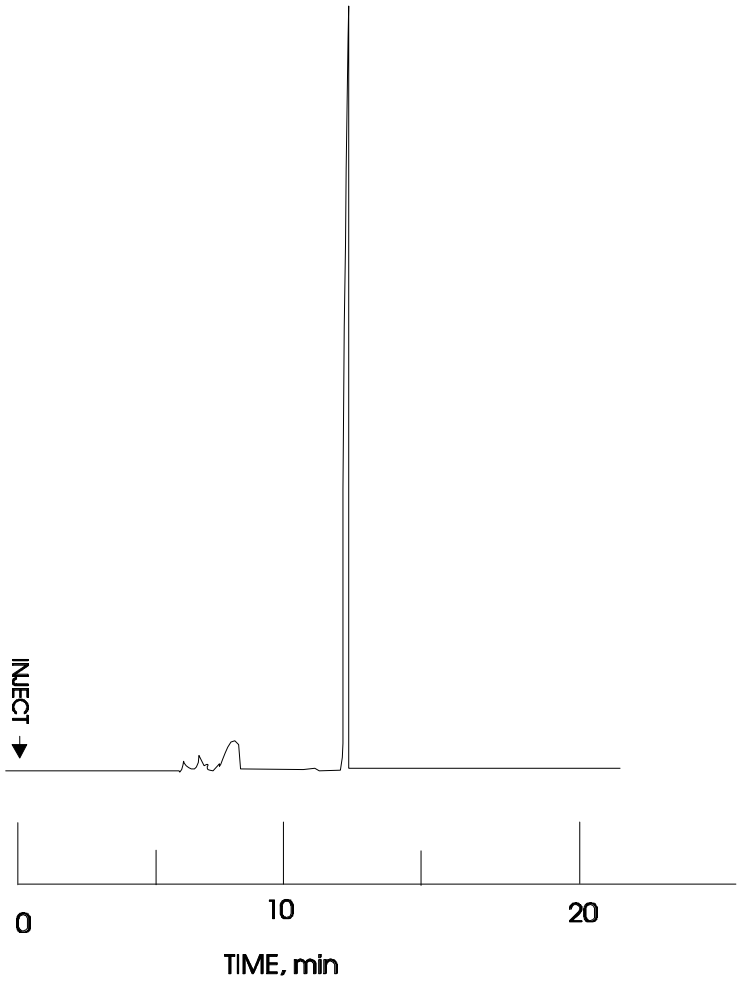

FIGURE 4 (A)
RECORDING AND REPORTING - SAMPLING RUN DATA RECORD
(**NOTE**: Only one sample run per data sheet)

Run # : _____ Project # : _____

Location : _____ Source Name : _____

Date Sampled : _____ Operator : _____

	Clock Time	Rotameter Reading	Flow Rate, Q mL/min	Impinger Temp. °F	Stack Temp. °F	Comments
0						
1						
2						
3						
4						
5						
6						

Chain of Custody (C.O.C.) Record Numbers, Sample Id. Numbers, Tare Weights, and Final Weights

Suggested Codes:

I & V w/ id. # ≡ Impinger, Transport, & Extraction Vial (all)

IMP w/ id. # ≡ Impinger (only)

E & T w/ id. # ≡ Extraction and Transport Vial (both)

NOTE: Indelible marks may be used subject to the warning in Section 8 of Method 430.

C.O.C. #	Sample Id. #	m_{tare} (tare weight)	m_{final} (final weight)

FIGURE 4 (B)
RECORDING AND REPORTING - CHAIN OF CUSTODY SAMPLE RECORD
(**NOTE**: Only one sample per data sheet)

Chain of Custody Log Record # : _____ Sample Id. # : _____

Run # : _____ Project # : _____

Location : _____ Source Name : _____

Date Sampled : _____ Operator : _____

Procedure	Date	Time	Given By	Taken By

Related Id. # (s)	Notes: (Include all unusual observations.)

FIGURE 4 (C)
RECORDING AND REPORTING - CHAIN OF CUSTODY LOG RECORD

PROJECT # : _____

Log Record #	Sample Id. #	Date	Time	Comments	Sample Type	Given By	Taken By