NCASI METHOD IM/CAN/WP-99.02

IMPINGER/CANISTER SOURCE SAMPLING METHOD FOR SELECTED HAPS AND OTHER COMPOUNDS AT WOOD PRODUCTS FACILITIES

NCASI SOUTHERN REGIONAL CENTER
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IMPINGER/CANISTER SOURCE SAMPLE METHOD FOR SELECTED HAPS AND OTHER COMPOUNDS AT WOOD PRODUCTS FACILITIES

1.0 Introduction

This test method was revised in December 2005. Numerous changes have been made with the vast majority related to quality assurance procedures, calculations, and criteria. The primary intent of the changes is to provide the sampling contractors some flexibility in the rather stringent quality assurance requirements.

This test method is intended to measure a select group of organic compounds that may be present in air emissions from stationary sources at wood products facilities. The organic compounds are captured in water filled impingers and an evacuated air sample canister. The analysis of the impinger contents is performed by gas chromatography/flame ionization detection and a colorimetric method. The analysis of the air sample canisters is performed by gas chromatography/mass selective detection, as well as gas chromatography/flame ionization detection.

Procedural steps outlined by this method range from optional to mandated. Actions that are not to be performed are also specified. The following terms will be used within the text of this method in order to clarify these activities:

Term:	The action, activity, or procedural step is…
…must not….	Prohibited
…may…	Optional
…should…	Suggested
…must…	Required

This NCASI impinger/canister sampling system is capable of accurately measuring a large number and wide variety of organic compounds in forest products industry source exhausts. Development of this wide applicability, however, resulted in a complicated field sampling system, lab analyses, and source concentration calculations. This revision to the method incorporates numerous quality control and quality assurance procedures intended to provide mills, sampling contractors, and laboratories clear feedback on the quality of sampling conducted.

This method has not been field validated via EPA Method 301 and is considered a self-validating method.

NCASI strongly suggests that sampling contractors and laboratories conduct train spikes and conduct full trial runs of all sample train configurations prior to use of this method in the field. Failure to do so will greatly increase the probability that quality assurance criteria will not be achieved.

NCASI recommends that mills, sampling contractors, and laboratories carefully review this method and all quality assurance procedures and criteria prior to source sampling. Since spikes will be used as one of the quality assurance procedures, evaluation of source concentration for the analytes of interest needs to be carefully undertaken prior to formulation of the spike solutions. If multiple and varied sources (for example, inlets and outlets of control systems) are to be sampled, multiple spike solutions or varied spike volumes will likely be necessary to meet spiking criteria.

This method shall be considered conducted only if all quality assurance procedures have been performed and the results clearly reported in the sampling report. Sufficient data must be presented such that the QA results and calculations are transparent.

2.0 Applicability

This method is applicable to determining the concentration of a select group of organic compounds from stationary air emission sources at wood products facilities. The select group of organic compounds listed in Table 2.1 includes hazardous air pollutants (HAPs), terpene compounds, acetone, and cis-1,2-dichloroethylene.

This method has been structured to allow for the determination of only the desired compounds of interest. While Table 2.1 provides a complete list of the compounds that are applicable, this method can be utilized for smaller sets of compounds such as for "Total HAPs" (acetaldehyde, acrolein, formaldehyde, methanol, phenol and propionaldehyde) as defined by the Environmental Protection Agency (EPA) for the wood products industry. For this case, only three of the four analytical procedures included in this method will be required to obtain the concentration of total HAPs in the source gas being tested.

This method is not applicable for any emission source that has a moisture content greater than 60% - by volume.

3.0 Overview of Sampling Method and Detection Limits

3.1 Field Sampling System

A sample of source gas is drawn through three midget impingers, each containing chilled organic free water. A Teflon-headed pump and a critical orifice are used to maintain a constant flow through the impingers. A portion of the gas exiting the impingers is drawn into an evacuated, inert stainless steel canister to capture the compounds not trapped in the aqueous impingers.

3.2 Laboratory Methodology

The water from the impingers is analyzed by direct injection into a gas chromatograph equipped with a flame ionization detector (GC/FID), referenced as [AQU] in this method.

The formaldehyde concentration in the impinger solution is determined by the acetylacetone procedure, referenced as [FOR] in this method. This procedure involves the reaction of formaldehyde with acetylacetone to produce a colored derivative which is measured by colorimetric analysis.

Table 2.1. Target HAP and Non-HAP Analytes Analysis Techniques

Analytes of Interest: HAPs	Impinger Analysis Technique	Canister Analysis Technique
acetaldehyde	[AQU] GC/FID	[MSD] GC/MSD
acrolein	[AQU] GC/FID	[MSD] GC/MSD
benzene		[MSD] GC/MSD
bromomethane		[MSD] GC/MSD
chloroethane		[MSD] GC/MSD
chloroethene		[MSD] GC/MSD
1,2-dichloroethane		[MSD] GC/MSD
formaldehyde	[FOR] Colorimetric	
methanol	[AQU] GC/FID	[MSD] GC/MSD
methyl ethyl ketone	[AQU] GC/FID	[MSD] GC/MSD
methyl isobutyl ketone	[AQU] GC/FID	[MSD] GC/MSD
methylene chloride		[MSD] GC/MSD
phenol	[AQU] GC/FID	[MSD] GC/MSD
propionaldehyde	[AQU] GC/FID	[MSD] GC/MSD
styrene		[MSD] GC/MSD
toluene		[MSD] GC/MSD
1,2,4-trichlorobenzene		[MSD] GC/MSD
m,p-xylene		[MSD] GC/MSD
o-xylene		[MSD] GC/MSD
Analytes of Interest: Terpenes		
cumene		[TER] GC/FID
camphene		[TER] GC/FID
3-carene		[TER] GC/FID
p-cymene		[TER] GC/FID
limonene		[TER] GC/FID
p-mentha-1,5-diene		[TER] GC/FID
alpha-pinene		[TER] GC/FID
beta-pinene		[TER] GC/FID
Other Organic Analytes of Interest:		
acetone	[AQU] GC/FID	[MSD] GC/MSD
cis-1,2-dichloroethylene		[MSD] GC/MSD

Terpenes in the canister are measured by a separate procedure from the one used for the non-terpene analytes captured in the canister. The terpene concentration is determined by drawing a sample from the canister into a gas loop. The sample is then directly injected into a GC/FID, referenced by [TER] in this method. The concentration of the remaining organic compounds is obtained by drawing another sample from the canister for pre-treatment by a cryogenic preconcentrator. The sample is then injected into a gas chromatograph equipped with a mass selective detector (GC/MSD), referenced as [MSD] in this method.

Figure A1 provides a diagram of the four analytical procedures covered by this method.

3.2.1 Interferences – Compounds present in the source gas can coelute with the analytes of interest during the chromatographic analysis. For example, if the proper chromatography conditions are not established, acrolein and ethanol may co-elute on the GC/FID chromatogram. These types of interferences can be reduced by the appropriate choice of GC columns, chromatographic conditions, and detectors. Method interferences may also be caused by contaminants in solvents, reagents, glassware and other sample processing hardware.

3.2.2 Stability – A formal stability study has not been performed, but laboratory tests show that the impinger catch is stable for approximately 2 weeks if kept refrigerated, at which time acrolein begins to degrade. At room temperature, the acrolein in the impinger catch degrades in a matter of hours. The canister catch, in general, is stable for 3 weeks.

3.2.3 Validation – This method is a self-validating method. The quality assurance procedures outlined in this method are designed to validate the performance of the measurement system by the introduction of spike solutions, a check of calibrations using standard solutions, and other measures. This method has not been evaluated using the United States Environmental Protection Agency (EPA) Method 301, Field Validation of Emission Concentrations from Stationary Sources (Appendix A to CFR 63).

3.2.4 Analytical Sensitivity – The sensitivity of each analytical instrument will tend to vary depending on characteristics of the laboratory equipment, analysis procedure, and compound being analyzed. This method, therefore, has not established one overall level of sensitivity for the analytes present in both the impinger and canister samples. Instead, different sensitivity requirements have been established for the [AQU], [FOR], [MSD], and [TER] analytical procedures.

3.2.4.1 [AQU] Method Detection Limit – This method will require that a method detection limit (MDL) be established for each compound detected by the [AQU] analytical procedure. MDLs must be established as defined by EPA[1], and the documentation should be kept on file for

[1] Federal Register, Part VIII, EPA, 40 CFR Part 136, Rules and Regulations, "Appendix B to Part 136-Definition and Procedure for the Determination of the Method Detection Limit"

reference. The MDL determined for each compound must be clearly reported for this method in terms of the laboratory concentration obtained in the aqueous sample (e.g. milligrams per liter, mg/L).

As an example, NCASI conducted a formal detection limit study to establish the [AQU] method detection limits in the source gas tested (based on 75 mL volume of aqueous impinger sample and 400 mL/min sample rate) for the compounds shown in Table 2.1 and listed below in Table 3.1.

Table 3.1. Example of MDLs

Analyte	NCASI Method Detection Limit (ppmv)
acetaldehyde	0.26
acrolein	0.16
methanol	0.35
methyl ethyl ketone	0.16
methyl isobutyl ketone	0.09
phenol	0.21
propionaldehyde	0.18
acetone	0.18

3.2.4.2 [FOR] Method Detection Level – The laboratory sensitivity level for formaldehyde analysis will be determined in a similar manner as the procedure used to determine the [AQU] MDLs. The formaldehyde MDL must be clearly reported in terms of mg/L in the aqueous sample (or equivalent units).

As an example, the formal detection limit study conducted by NCASI established that the MDL for formaldehyde in the source gas tested (based on 75 mL volume of aqueous impinger sample and 400 mL/min sample rate) was 0.13 ppmv.

3.2.4.3 [MSD] Measurement Level – A formal detection limit study will not be required to establish the level of sensitivity for the compounds determined by the [MSD] analytical procedure. Instead, the measurement level (ML) established for these compounds will be set at 50 parts per billion by volume (ppbv) in the canister. This ML will be verified by the lowest calibration standard. If the analyte of interest is detected by the GC/MSD below the ML, report the concentration as <50 ppbv.

Note that the canister sample may or may not require dilution prior to the [MSD] analytical procedure. If the canister sample is diluted, then the actual source gas concentration will have to be adjusted for dilution. Clearly report the ML, the dilution factor (if applicable), and the source gas detection level.

NCASI used approximately a 2:1 dilution ratio for the canister analysis. Using the 50 ppbv as the ML for the diluted result, the actual detection level for the analytes in the source gas is approximately 100 ppbv. Using a 50 ppbv ML for the canister will help limit the number of cases in which a polar analyte is measured in the canister but not in the impingers.

3.2.4.4 [TER] Measurement Level – The laboratory sensitivity level for terpene analysis will be based on the measurement level of the lowest calibration standard or 1000 ppbv. If the analyte of interest is detected by the GC/FID below the ML, report the concentration as <1000 ppbv. The terpene samples are generally diluted, therefore the ML of the canister sample will have to be adjusted for dilution. Clearly report the ML, the dilution factor (if applicable), and the source gas detection level.

3.2.4.5 Treatment of Values Below the Detection Limits (Non-Detects) - Since the sampling train for this method has two sample sections, the impingers and the canisters, sometimes a compound will be measured below detection limits in one section but not in the other section. Nine of the compounds listed in Table 2.1 are measured in both the canister and the impinger section of the sample train.

This method does not recommend a treatment for non-detects. However, it is recommended that compound characteristics and the behavior of compounds within the sampling system be considered relative to treatment of non-detects. For the nine compounds rarely will the canister 'catch' exceed 20% of the total compound capture. More commonly, the canister catch will be 5% or less of the total catch since all nine of these compounds are highly soluble in water.

As explained in a subsequent section of the method, NCASI established a Measurement Level of 50 ppbvd for the (non-terpene) compounds in the canister to reduce the frequency of samples that would be "detect" in the canister but non-detect in the impingers. The result of this is that if one of the nine compounds reaches a level of 50 ppbvd in the canister, it often will occur at detectable levels in the impinger solution.

4.0 Apparatus

4.1 Field Sampling

A diagram of the sample collection train is shown in Figure A2. Alternative configurations for the collection train and components may be used, but the user must demonstrate the validity of the alternative configuration by achieving the self-validating quality assurance criteria in Section 7.

4.1.1 Heated Sample Probe – The sample probe is constructed of 1/2 inch OD stainless steel tubing or equivalent. For wood products sources, the probe is maintained at 250 ± 25°F. The probe inlet is placed near the center of the stack or duct.

4.1.2 Heated Filter Box – The heated probe is directly connected to a heated box containing a Teflon filter. The filter housing and connections are made of stainless steel. A thermocouple connected to or within the filter housing is used to record the filter temperature which must be maintained at 250 ± 25°F.

4.1.3 Sample Line – An unheated Teflon line is used to convey the sample from the back of the heated filter box to the first impinger.

4.1.4 Midget Impingers – The sample line is connected to three midget impingers in series. The first impinger is equipped with a stem that has a frit on the end to improve gas/liquid contact. The following two impingers have regular tapered stems. All impinger train connectors should be glass, Teflon, or an equivalent inert material.

4.1.5 Filter – A second Teflon filter may be used after the impingers to prevent any fiber, debris, or water from accidentally being drawn into the critical orifice.

4.1.6 Variable Area Flow Meter – A flow meter should be placed in line after the impingers for a flow check during sampling.

4.1.7 Flow Control Device – A critical orifice or other equivalent device must be used to maintain a steady flow rate through the collection train. The flow rate must be 400 ± 100 mL/min.

4.1.8 Vacuum Gauges – Two vacuum gauges should be placed on each side of the critical orifice capable of reading 25 inches of mercury gauge (in Hg).

4.1.9 Teflon Head Pump – The critical orifice is followed by a pump, with a Teflon head, capable of providing a vacuum of about 18 in Hg. Pump capacity must be sufficient to obtain and maintain critical conditions at the orifice. The Teflon diaphragms used in the pump must be cleaned or replaced prior to each mill test effort.

4.1.10 Canister Sample Pickup Point – A tee with an on/off valve must be placed in line between the sample pump exhaust and the excess source gas vent for the pump. The canister will draw a slip-stream of source gas at this location.

4.1.11 Variable Area Flow Meter with a Flow Controller – A flow meter should be placed in line before the canister as a visual aid for maintaining the sample delivery rate to the canister during sampling. The flow to the canister will require adjustment periodically during sampling to ensure that the canister is filled at a constant rate over the sample run. The flow controller can be a needle valve.

4.1.12 Canisters – A 6 L SUMMA™ polished canister or 6 L SilcoSteel™ canister is used to collect a portion of the sample gas. Other types of canisters can be used if the canisters are shown to have similar non-reactive properties.

4.1.13 Thermometer – An accurate thermometer is used to measure the ambient and canister temperatures.

4.1.14 Canister Gauge – An absolute pressure gauge or a vacuum gauge capable of indicating ±0.1 in. Hg is placed after the canister sample pickup point and before the canister. This gauge will indicate the canister pressure before and after the sample run as well as during the leak check procedure. If an absolute pressure gauge is used, then the barometric pressure can be obtained before and after each sample run.

4.1.15 Sample Storage Bottles – Glass (e.g., VOA vials) or polyethylene bottles can be used to store the aqueous impinger samples.

4.2 [AQU] GC/FID Analysis

4.2.1 Laboratory Glassware – Use volumetric pipets, volumetric flasks, 2.0 mL autosampler vials, and syringes necessary for standards preparation and analysis.

4.2.2 Gas Chromatography System – Use a gas chromatography analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories including an autosampler, syringes, analytical columns and gases. **The autosampler must be capable of maintaining the samples at 4°C to prevent degradation of acrolein.**

4.2.3 Column – Use a 60 m (or longer) x 0.53 mm x 3 μm bonded phase DB-624 fused silica capillary column (J&W Scientific or equivalent), or another column shown to be capable of separating the analytes of interest.

4.2.4 GC Detector – This is a flame ionization detector with an appropriate data acquisition system.

4.3 [FOR] Formaldehyde Analysis

4.3.1 Laboratory Glassware – Use borosilicate test tubes (5 to 10 mL) with TFE-fluorocarbon-lined screw caps, 50 mL buret, volumetric pipets, volumetric flasks, syringes, and cuvettes necessary for standards preparation and analysis.

4.3.2 Spectrophotometer – A spectrophotometer should be capable of measuring absorbance at a 412 nm wavelength.

4.3.4 Absorption Cell – The absorption cell must have a minimum path length of 1.0 cm. Longer paths may be used to improve the sensitivity of the photometer.

4.3.5 Heating Block – A heating block or water bath should be regulated to maintain 60°±3°C for the test tubes.

4.3.6 Centrifuge with Capped Tubes

4.3.7 Magnetic Stirrer and Stir Bars

4.3.8 pH Meter – The meter should conform to the requirements of ASTM Test Method D 1293.

4.4 [MSD] GC/MSD Analysis

4.4.1 Laboratory Glassware – Use volumetric pipets, volumetric flasks, and syringes necessary for standards preparation and analysis.

4.4.2 Cryogenic Concentration System – A cryogenic preconcentrator **capable of trapping polar compounds** is required to concentrate the sample prior to introduction into the GC/MSD system.

4.4.3 Gas Chromatography System – Use a gas chromatography analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories including syringes, analytical columns and gases.

4.4.4 Column – Use a 60 m (or longer) x 0.32 mm x 0.25 µm bonded phase DB-624 fused silica capillary column (J&W Scientific or equivalent), or another column shown to be capable of separating the required analytes.

4.4.5 Mass Selective Detector – Use a mass selective detector capable of scanning from 29 amu to 300 amu every 2 seconds or less using 70 volts electron energy in the electron impact ionization mode (or equivalent), and an appropriate data acquisition system.

4.5 [TER] GC/FID Analysis

4.5.1 Laboratory Glassware – Use volumetric pipets, volumetric flasks, and syringes necessary for standards preparation and analysis.

4.5.2 Sample Loop Injection System – Use a system capable of extracting a sample from the canister into a sample loop. The sample is then directly injected into the GC/FID system.

4.5.3 Gas Chromatography System – Use a gas chromatography analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories including syringes, analytical columns and gases.

4.5.4 Column – Use a 30 m x 0.32 mm x 0.25 µm bonded phase DB-1 fused silica capillary column (J&W Scientific or equivalent), or another column shown to be capable of separating the terpenes of interest.

4.5.5 GC Detector – Use a flame ionization detector with an appropriate data acquisition system.

5.0 Reagents

5.1 DI Water

Organic free or deionized (DI) water is used in the impingers as a capture solution for rinsing the sample line and impingers at the end of the sample run, and for preparation of all aqueous calibration standards and spike solutions.

5.2 Nitrogen Gas

Pure nitrogen gas (99.999%) must be used for cleaning the canisters and as the dilution gas for gas calibration standards and spike solutions. When preparing the gas calibration standards and spike solutions, the nitrogen gas must be humidified by bubbling through DI water prior to addition to a canister.

5.3 Purity of Reagents

Reagent grade chemicals shall be used for all tests. The reagents required by this method shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the highest purity grade available.

5.4 [AQU] Primary Stock Solution

Reagent grade chemicals must be used in the preparation of the aqueous primary stock solution for the [AQU] GC/FID analysis portion of this method. Prepare the [AQU] Primary Stock Solution by combining aliquots of the compounds of interest listed in Table 5.1 in a 100 mL volumetric flask. Dilute to 100 mL with DI water. This stock solution will be used to prepare the [AQU] Calibration Standards and the [AQU] Spike Solution. The resulting [AQU] Primary Stock Solution will have a concentration of 1000 mg/L.

Table 5.1. Reagents for the [AQU] Primary Stock Solution

Compound	Amount (µL) to Add to 100 mL Volumetric Flask
acetaldehyde	128
acetone	128
acrolein	119
methanol	126
methyl ethyl ketone	124
methyl isobutyl ketone	125
propionaldehyde	124
phenol (solid)	100 mg

5.5 [AQU] Calibration Standards

Prepare a series of aqueous calibration standards from the [AQU] Primary Stock Solution to develop a calibration curve for each compound of interest. The lower limit [AQU] Calibration Standard must be 0.5 mg/L. The upper limit of the aqueous calibration standards should be 1000 mg/L.

5.6 [AQU] Internal Standards

The aqueous internal standard is added to every standard, blank, matrix spike, and sample before analysis to compensate for variations in sample size and is used in determining relative response factors for the target compounds analyzed by the [AQU] GC/FID procedure used in this method. The recommended [AQU] internal standard for this method is cyclohexanol. Another internal standard that may be used in place of cyclohexanol is 2,2,2-triflouroethanol.

5.6.1 [AQU] Internal Standard Stock – This internal standard will be added to each laboratory blank, quality control sample and calibration standard. If cyclohexanol is to be added to autosampler vials, prepare the aqueous internal standard stock solution by using 0.312 mL of pure cyclohexanol and diluting to

100 mL with DI water in a 100 mL volumetric flask. The resulting concentration of this stock solution will be 3000 mg/L cyclohexanol.

5.6.2 [AQU] Intermediate Internal Standard – This internal standard will be added to each field sample bottle along with a known volume of DI water in the laboratory prior to sampling. If using cyclohexanol, prepare this intermediate internal standard by using 3.12 mL of pure cyclohexanol and diluting to 2.0 L with DI water in a 2.0 L volumetric flask. The resulting concentration of this internal standard will be 1500 mg/L cyclohexanol. (Note that Equation 9.2 in Section 9 assumes addition of cyclohexanol to the field sampling solution.)

5.7 [FOR] Primary Stock Solution

For this method, the preparation of the primary stock solution for formaldehyde will be based on the ASTM Method D 6303-98, "Standard Test Method for Formaldehyde in Water." The formalin solution called for by the ASTM method contains 37% formaldehyde by weight or 40g formaldehyde/100 mL formalin solution. Note that formalin solutions contain methanol, and addition of formalin to spike solutions will alter the methanol concentration.

The [FOR] Primary Stock Solution is made by placing a 2.7 mL aliquot of formalin solution (37% formaldehyde by weight) in a 1000 mL volumetric flask and diluting to 1000 mL with DI water. The formalin solution must be standardized per the ASTM method to verify the formaldehyde content. The primary stock solution should be stored at room temperature, in the dark, and must be standardized every six months. The solution appears to be reasonably stable.

5.8 [FOR] Intermediate Stock Solution

The intermediate stock solution must be prepared from the [FOR] primary stock solution each time the calibration standards are prepared. Prepare the [FOR] intermediate stock solution by placing a 1.0 mL aliquot of the [FOR] primary stock solution in a 100 mL volumetric flask and dilute to 100 mL with DI water. The resulting [FOR] intermediate stock solution will have a formaldehyde concentration of 10 mg/L.

5.9 [FOR] Calibration Standards

The spectrophotometer used in the colorimetric analysis procedure must be calibrated using six different formaldehyde concentrations. The calibration standards will be prepared in six screw-capped test tubes. Leave the first test tube empty and place 0.1, 0.2, 0.4, 1.0, and 1.5 mL of the [FOR] secondary stock solution in the second through sixth test tubes, respectively. Fill all six test tubes to 2.0 mL with DI water. The resulting concentrations in the test tubes will be 0.0, 0.5, 1.0, 2.0, 5.0, and 7.5 mg/L formaldehyde, respectively.

5.10 [FOR] Acetylacetone Reagent

Prepare by dissolving 15.4 g of ammonium acetate in 50 mL of DI water in a 100 mL volumetric flask. To this solution, add 0.20 mL of pure acetylacetone and 0.30 mL of aldehyde-free glacial acetic acid (specific gravity 1.05). Mix thoroughly and dilute to 100 mL with DI water. This reagent must be stored in a brown glass bottle and refrigerated. This reagent is stable for a maximum of two weeks.

5.11 [MSD] Primary Stock Gas Mixtures and Calibration Standards

The compounds that are analyzed by the GC/MSD technique are either purged from, partially purged from, or not quantitatively captured in the aqueous impinger sample. As a consequence, two separate primary stock mixtures will be required to prepare the calibration standards for the GC/MSD analytical technique. In either case, the primary stock mixtures shall consist of the compounds of interest that will be captured in the canister.

5.11.1 [MSD] Aqueous Analyte Primary Stock Gas Mixture – This primary stock gas mixture shall consist of the compounds of interest that have the potential to be purged from the aqueous impinger sample. These compounds are analyzed by both the [AQU] and [MSD] procedures. This primary stock gas mixture is made in two steps. First an aqueous solution is prepared and then an aliquot of the aqueous solution is converted to a gas mixture.

The aqueous solution is prepared by adding the aliquot for each compound of interest shown in Table 5.2 into a 100 mL volumetric flask. Dilute this solution to 100 mL with DI water, then inject 10 µL of this aqueous stock solution into a clean evacuated canister (below 1.0 in Hga) along with 170 µL of DI water. Fill the canister to 60 in Hga with a nitrogen gas. The resulting concentration for each compound in the [MSD] aqueous analyte primary stock solution will be 1000 ppbv in the canister.

5.11.2 [MSD] Aqueous Analyte Calibration Standards – Prepare a series of gas calibration standards for the [MSD] analysis technique. The lower limit of the gas calibration standards must be 50 ppbv. The upper limit of the gas calibration standards should be 500 ppbv. The concentration of each calibration standard shall be prepared by adding the appropriate amount of [MSD] aqueous analyte primary stock gas mixture to a clean evacuated (<1.0 in Hga) canister and diluting with nitrogen gas to 40 in Hga or above.

5.11.3 [MSD] Gas Analyte Primary Stock Gas Mixture – This primary stock gas mixture shall consist of the compounds in Table 2.1 that are not captured in the aqueous impinger sample as indicated by the [MSD] analysis technique only. The compounds of interest can be obtained in gas phase directly. Refer to EPA Compendium Method TO-14 for a possible list of available compounds.

Table 5.2. Reagents for the [MSD] Aqueous Analyte Primary Stock Solution (gas phase)

Compound	Amount (µL) to Add to 100 mL Volumetric Flask
acetaldehyde	281
acetone	369
acrolein	334
methanol	202
methyl ethyl ketone (2-butanone)	448
methyl isobutyl ketone	628
propionaldehyde	360
phenol (solid)	471 mg

The concentration of each compound should be 1000 ppbv at a certified level of Environmental Protection Agency (EPA) Traceability Protocol Number 1 or other approved certified level.

5.11.4 [MSD] Gas Analyte Calibration Standards – Prepare a series of gas calibration standards for the [MSD] analysis technique. The lower limit of the gas calibration standards must be 50 ppbv. The upper limit of the gas calibration standards should be 500 ppbv. The concentration of each calibration standard shall be prepared by adding the appropriate amount of [MSD] gas analyte primary stock gas mixture to a clean evacuated (<1.0 in Hga) canister and diluting with nitrogen gas to 40 in Hga or above.

5.12 [MSD] Internal Standard

An internal standard must be added to the gas samples analyzed by the GC/MSD technique. The commonly used internal standards are bromochloromethane, 1,4-diflourobenzene, and d5-chlorobenzene. For additional guidance, refer to EPA Compendium Method TO-14.

The gas concentration of the [MSD] internal standard will be at an appropriate level as determined by the laboratory conducting the analysis with a recommended concentration range between 100 and 300 ppbv.

5.13 [TER] Primary Stock Gas Mixture

The primary stock gas solution for the terpene compounds will be used to make calibration standards for the [TER] GC/FID analysis technique in this method. This stock solution is prepared in two steps. First add the amount of each terpene compound of interest shown in Table 5.3 into a 10 mL volumetric flask and dilute to 10 mL with

reagent grade ethyl ether. Then inject 100 μL of the terpene/ethyl ether solution into a clean evacuated canister (below 1.0 in Hga). Fill the canister to 60 in Hga with nitrogen gas. The resulting [TER] primary stock solution will have a canister concentration of 100 ppmv for each terpene compound.

Table 5.3. Reagents for the [TER] Primary Stock Solution

Compound	Amount (μL) to Add to 10 mL Volumetric Flask
p-mentha-1,5-diene	810
3-carene	786
cumene	694
p-cymene	780
limonene	811
α-pinene	795
β-pinene	793
camphene (solid)	681 mg

5.14 [TER] Calibration Standards

Prepare a series of calibration standards from the [TER] Primary Stock Solution. The calibration standards will be used to develop a calibration curve for each terpene compound of interest. The lowest calibration standard must have a concentration of 1.0 ppmv. The highest calibration standard should be 300 ppmv. For each concentration, the appropriate amount of [TER] Primary Stock Solution shall be added to a clean evacuated gas cylinder (below 1.0 in Hga) and diluted with nitrogen gas to 60 in Hga.

5.15 Spike Solutions

This method requires that quality assurance procedures be carried out to ensure that the measurement system is capable of capturing the compounds of interest from the emission source and preserving those compounds until analysis can be conducted. Spike solutions are used to introduce a known quantity of reagent(s) into the measurement system operating under normal sampling conditions. The spike samples are collected and analyzed along with the source samples collected by the measurement system.

5.15.1 Aqueous Spike Solution – The aqueous spike solution shall contain the appropriate amount of each compound of interest such that the equivalent spiking level criteria provided in Table 7.2 are achieved. Equivalent spiking level is defined in Section 7.5.3 and spiking procedures are discussed in Section 7. The expected source gas concentration can be obtained from historical test results, test results from similar emission sources, or published emission factors. The NCASI

public web site also provides a database of compound concentrations at wood products sources (www.ncasi.org).

The aqueous spike solution must be protected against compound degradation. This solution should be formulated no earlier than 4 days prior to the first day of testing, and the solution should be kept on ice or refrigerated continuously. It is recommended that a field spike (Section 7.3) be prepared when the spike solution is first formulated and that this solution be analyzed within 24 hours of preparation. The analysis results can then be compared to the field spikes made during testing.

This method allows the use of a single spike solution closely targeted to match the source concentration of the compounds of interest or two spike solutions intended to bracket the compound concentrations. The use of spikes and the calculation of their recovery are discussed in detail in Section 7.

It is recommended that the volume of the aqueous spike introduced into the run spike (Section 7.5) and train spike (Section 7.6) be 1.0 mL for convenience and ease of use. Other spike volumes are also acceptable.

5.15.2 Prepare Gas Spike Solution – The gas spike shall contain the appropriate concentration of each compound of interest to yield concentrations in the canister similar to those in the source gas. The expected source gas concentration can be obtained from historical test results, test results from similar emission sources, or published emission factors.

The gas spike solution can be prepared by diluting the [MSD] gas analyte primary stock gas mixture, the [TER] primary stock gas mixture, or purchasing cylinders with the compounds of interest at the desired concentrations. The gas mixtures can then be diluted or stored undiluted in a cleaned canister that is pressurized between 40 and 60 in Hga that will be used as a spike transfer container.

5.16 Second Source or Reference Standard

A reference standard is used to validate each calibration curve developed for the analytical procedures in this method. The reference standard can be certified or from a secondary source. A second source reference standard is purchased from a different vendor than was used to purchase the reagent used to make the primary stock solution.

The concentration for each second source or reference standard shall be equivalent to the midpoint of the reagent's calibration curve. Note that an aliquot of internal standard solution must be added to the second source or reference standard prior to analysis.

6.0 Sample Procedure

Reliable emission data can be obtained through properly configuring and operating the sample collection train. Quality assurance measures provide verification that appropriate sampling techniques were utilized. This section will describe the assembly and operation of the sample collection train. Quality assurance requirements are discussed in Section 7.

6.1 Preparation of the Sample Bottles

Add 1.0 mL [AQU] intermediate internal standard stock to each sample bottle and dilute with 74 mL of DI water. Record the pre-sample weight of each bottle.

6.2 Sample Run

This is a sample collection period preceded and followed by quality assurance checks (such as leak checks and flow checks) as specified in this method. It is recommended that the duration of each sample run be one hour. Sampling or source specific conditions may require, however, that the collection time be adjusted to a shorter or longer interval.

For source types with multiple vents such as press vents, a sample run may refer to all collection trains that operate simultaneously. Control device inlets and outlets are considered separate sources.

6.3 Sampling Event and Mill Visit

A sampling event is defined as three consecutive sample runs conducted at one source type. A mill visit is defined as all sampling that occurs between arrival and departure of the test team to a facility or mill.

6.4 Preparation of the Collection Train

Prior to testing each new emission source, clean the probe and filter housing with DI water and replace the filter. Use one pre-weighed sample bottle for each impinger set. Record the ID of the sample bottle and divide the contents between the three midget impingers so that each contains approximately 25 mL of the aqueous solution.

Assemble the impinger/canister collection train as shown in Figure A2. For sources that are expected to have very high amounts of moisture (40% to 60%-by volume), a fritless empty impinger can be used as the first impinger (for a total of four impingers) to act as a water drop-out. Keep both the impingers and canister out of direct sunlight. Attach a thermocouple to the outside of the canister and keep the canister valve closed.

6.5 Leak-Check Procedure

An optional leak check can be conducted when the collection train is first assembled before the system is brought up to operating temperature. A leak check prior to starting the sample run is mandatory with the collection train at operating temperature.

The method used for leak checking the collection train will be dependent on the configuration of the train. The collection train shown in Figure A2, for instance, has two sections to leak check; the probe/impinger section and the canister section. The probe/impinger section includes components from the probe to the pump. The canister section is from the canister sample pickup point to the canister.
The probe/impinger section and the canister section will have an acceptable leak check when the loss of vacuum is not greater than 1.0 in Hg over a 2.0 minute period.

6.5.1 Probe/Impinger Section Leak Check – The leak check procedure shall be conducted when all of the heated components have reached operating temperature (250°F ± 25°F). The probe and impinger section of the collection train is leak checked by turning on the sample pump, plugging the probe tip, and drawing a vacuum of at least 15 in. Hg. After 15 in. Hg has been reached, close the inlet side of the sample pump and turn the sample pump off. After the pressure reading has stabilized, note the beginning and ending pressure on the vacuum gauge over a two minute period.

6.5.2 Leak Check Troubleshooting – The presence of bubbles in the first impinger indicates a leak located between the probe and the first impinger: a leak between the impingers or behind the impingers will be indicated by aqueous solution being drawn up one of the impinger stems (flow direction is backwards through the system).

When this section of the collection train has passed the leak check, ***slowly*** remove the plug at the probe tip. Bringing this section up to ambient pressure slowly will ensure that the aqueous solution remains distributed evenly between the impingers.

6.5.3 Canister Section Leak Check – Close the on/off valve at the canister sample pickup point. Open the needle valve of the flow meter to the canister. Open the canister valve and allow the canister to bring this section under vacuum. After the pressure reading in this section equalizes, note the beginning and ending pressure readings on the canister vacuum gauge over a two minute period. An alternative procedure might include a second evacuated canister that could be used to draw a vacuum on this section. This will alleviate the necessity for using the sample canister for leak checking.

If this section passes the leak check, close the canister valve and slowly open the on/off valve. There should be very little loss of vacuum (less than 0.5 in Hga) in the canister since the air volume in this section of the collection train is minimal.

6.6 Pre-Sample Run Procedures

6.6.1 Verify that the probe and filter housing are at operating temperature. Place crushed ice and water around the impingers.

6.6.2 Obtain the average of five flow rate readings taken at the probe tip of the collection train. The average flow rate should be 400 ± 100 mL/min. Record the ambient temperature and pressure at this measurement location.

6.6.3 Obtain the flow rate of the source gas at the test port using appropriate stack measurement methods. Other source gas parameters required must include stack gas temperature, moisture content, static pressure, and percent O_2 and CO_2.

6.6.4 Insert the probe into the test port and align it perpendicular to the source gas flow. Recheck the operating temperature. Close the on/off valve at the slip-stream pickup point for the canister sample, open the canister valve to verify that the canister pressure is less than 1.0 in Hga, and adjust the canister flow meter so that it is just barely open (this will prevent excessive flow to the canister at the start of the sample run). Record the beginning canister pressure and temperature.

6.7 Sample Collection

Prior to the start of each sample run, coordinate with process operators to verify that the production unit and source gas being tested are under steady state conditions.

The collection train will be started in two steps. The first step will involve purging ambient air from the collection train by drawing sample gas through the impingers. The second step will then establish sample flow to the canister.

6.7.1 Start the impinger sample pump. Record start time and flow rate at the flow meter.

6.7.2 After approximately one minute, open the on/off valve at the canister sample pickup point and adjust the flow rate to the canister. An appropriate flow rate will deliver a constant amount of sample gas over the entire sample run. For the 6 L canisters and a 1-hour sample run, it is recommended that the flow rate be approximately 100 mL/min. It is recommended that the canister sampling time exceeds 90% of the impinger sampling time.

6.7.3 At various intervals during the sample run, record the impinger flow rate, canister flow rate, and the canister pressure and temperature.

6.7.4 At the end of the sample run, turn off both the slip-stream valve and impinger sample pump. Record the ending canister pressure and temperature. <u>Close the canister valve.</u>

6.8 Post-Sample Run Procedures

6.8.1 Remove probe from test port.

6.8.2 Turn on the sample pump only long enough to obtain the average of five flow rate measurements at the probe tip.

6.8.3 Verify that the differences between pre- and post-average flow rate measurements are within 20%.

6.8.4 If the difference is greater than 20%, then examine the collection train and determine if the sample run is valid. A post-sample run leak check may be conducted in order to examine flow rate differences.

6.8.5 Obtain the flow rate of the source gas at the test port using appropriate stack measurement methods. Other source gas parameters required must include stack gas temperature, moisture content, static pressure, and percent O_2 and CO_2.

6.9 Sample Recovery

6.9.1 Disconnect the sample line at the exit to the heated filter box. Rinse the sample line with a small amount of DI water (approximately 10 mL). Operate the sample pump long enough to draw the rinse into the first impinger.

6.9.2 Transfer the contents of the impingers into the original sample bottle. Label the sample bottle appropriately, mark the water level, and obtain the post-sample weight of the bottle. For high moisture sources, two sample bottles can be used.

6.9.3 The sample bottles must be stored on ice or in a refrigerator set at approximately 4°C. If the water samples are required to be shipped to the laboratory for analysis, pack the sample bottles in ice or insulated frozen packs. (Direct contact with frozen packs can freeze the samples.)

6.9.4 Disconnect the canister sample line from the canister and place the protection cap on the canister valve. Label the canister appropriately. Ship the canisters in a container that will keep the canister valve protected.

7.0 Field Quality Assurance Procedures, Calculations, and Criteria

The quality assurance (QA) measures used to verify the performance of the collection train(s) include conducting duplicate sample runs, run spikes, train spikes, field spikes, and field blanks. A summary of the QA procedures is provided in the appendix. The duplicate and spiked sample trains are operated concurrently with a “normal” sample train. The results and calculations for all quality assurance procedures conducted must be

provided in the sampling report. Further, all information required for calculation of the QA results must be presented in the report so that the calculations are transparent.

7.1 Field Blank Sample

There should be at least one field blank sample per facility or mill tested. The field blank will be one of the pre-weighed sample bottles containing 75 mL of solution (DI water and internal standard). The field blank must be analyzed along with the other aqueous samples collected by this method. NCASI recommends that one field blank be prepared per day so that more than one blank is available for analysis.

7.2 Equipment Blank Sample

75 mL of DI water must be used to rinse the collection train components in the field and collected for analysis either prior to testing or between sample runs. Note that the internal standard will need to be added to the equipment blank at the laboratory prior to analysis. The equipment blanks must be analyzed along with the other aqueous samples collected by this method. At a minimum, one equipment blank shall be collected per sampling trip or mill visit.

7.3 Field Spikes

7.3.1 Aqueous Field Spike – For each run spike or train spike, prepare an aqueous field spike by injecting an aliquot (e.g., 1.0 mL) of aqueous spike solution (Section 5.15.1) into one of the sample bottles containing DI water and [AQU] Internal Standard. Aqueous field spikes should be made during or immediately after a run spike or a train spike. Clearly label the aqueous field spike and analyze with the corresponding aqueous sample from the run spike. Results of the aqueous field spike must be clearly reported.

The aqueous field spike analytical results must be used to calculate the amount of spike introduced. In other words, the mass of each compound in the aqueous field spike must be used as the mass of compound spiked for the purposes of spike recovery calculations.

7.3.2 Spiked Canisters and Gas Field Spike – Prior to going to the field, prepare two spiked canisters for each run spike. A spiked canister is prepared by injecting an aliquot, for example 25 mL at ambient pressure, of the gas spike solution (Section 5.15.2) into a clean evacuated canister. The gas spike solution can be transferred to each spike canister using a gas syringe with a valve. It is very important to use a consistent gas spike volume or record the volume of spike (both at ambient conditions) that is injected into each canister. Clearly label each spike canister.

A gas field spike will be required for each run spike. Choose one of the spiked canisters to be the gas field spike and label it as such. The gas field spike will be

analyzed along with the spiked canister used for the run spike. Results of the gas field spike must be clearly reported.

7.4 Duplicate Sample Run or Duplicate

One duplicate sample run must be conducted per mill visit or per sampling event for each source type at a mill, whichever is more stringent. The optimal sampling configuration used to conduct a duplicate sample will be to connect two separate collection trains to a single probe and filter box as shown in Figure A3. Two completely separate sample trains may also be used. Alternative configurations for conducting a duplicate sample run can be used if shown to meet the QA criteria. Duplicate sample trains must be configured such that independent leak checks and flow rate measurements can be conducted.

For source types with multiple emission points tested simultaneously such as press vents, this method requires that a duplicate sample run be conducted at only one of the emission points. To provide additional QA, however, it is recommended that duplicate samples be collected at more than one emission point during a sampling event. Control device inlets and outlets are considered separate sources.

7.4.1 Duplicate Sample Run Procedure - Prepare both collection trains as per Section 6.4. To leak check the duplicate train shown in Figure A3, disconnect one of the trains from the outlet of the heated filter box. Cap that connection and follow Section 6.5 to conduct the leak check procedure for the probe, filter box, and impinger/canister assembly for one train. For the disconnected impinger/canister train, again follow Section 6.5 but disregard the probe and filter portion of the leak check procedure.

Follow Section 6.5 through Section 6.8 to complete a duplicate sample run, making sure that both collection trains are started simultaneously and operate in a similar manner.

The results from the two sample trains are averaged and reported. If either or both sampling trains provide values below detection limits, the results should be reported according to the applicable regulation or as required by the regulatory authority. The sampling report must contain the individual results from the two sampling trains in the report's QA section.

7.4.2 Notes Regarding Duplicate Trains – (1) Leak checks of duplicate trains are a common source of field error. Make sure that the impinger trains are isolated prior to leak checks. (2) Both impinger trains for a duplicate sample run should start and end the sample run at approximately the same time. (3) The results from duplicate sample train sampling must be reported as an average of the two duplicate sample trains.

7.4.3 Duplicate Difference Criteria – Calculate the source gas concentration for each of the targeted compounds from the duplicate sample trains and determine the applicable duplicate difference criteria shown in Table 7.1.

Table 7.1. Duplicate Difference Criteria

If the average source gas concentration for the duplicate sample run is….	Then the duplicate difference should be…...
…less than 0.5 ppmvd	…..equal to or less than 50%
….between 0.5 to 1.5 ppmvd	….equal to or less than 40%
….greater than 1.5 ppmvd	….equal to or less than 30%

7.4.4 Duplicate Difference Calculation – Calculate the difference between the source gas concentration as determined by the normal and duplicate trains. This difference is calculated by the absolute value of the dry source concentration determined by one sample train minus the dry source concentration determined by the other sample train divided by the average dry source concentration determined from both trains (Equation 7.1). Note that the masses of the compounds collected in the two sample trains are not compared.

Equation 7.1

$$\%\,difference = ABS\left|\frac{\left(C_{SN} - C_{SD}\right)}{Average\left(C_{SN}, C_{SD}\right)}\right| \times 100$$

C_{SN} = dry source gas concentration determined by the normal train, ppmvd
C_{SD} = dry source gas concentration determined by the duplicate train, ppmvd

The result of the calculation is expressed as a percent difference. The duplicate difference is evaluated with respect to the criteria provided in Table 7.1. The criteria vary according to the concentration of the compound(s) in the source gas. The percent difference should not be calculated if the concentration of the analyte determined by either the normal train or the duplicate train is detected below the method detection limit.

Results of the duplicate sample runs must be clearly calculated and reported for each analyte. Sufficient data must be presented such that the QA results and calculations are transparent.

7.5 Run Spike

One run spike must be conducted per mill visit or per sampling event for each source type at a mill, whichever is more stringent. An alternative procedure is also provided that allows the use of bracketed spikes.

Spike solutions or gases should be within an appropriate range. This method provides criteria for Equivalent Spiking Levels in Tables 7.2 and 7.3. Spike solutions and spike gases should be considered well in advance of field sampling.

For source types with multiple emission points tested simultaneously, such as press vents, this method requires that a run spike be conducted at only one of the emission points. Control device inlets and outlets are considered separate sources.

If the analytes of interest are limited to acetaldehyde, acrolein, acetone, formaldehyde, methanol, phenol, methyl ethyl ketone, methyl isobutyl ketone, and propionaldehyde, then substitute an unspiked evacuated canister for the spiked canister.

Alternative configurations for conducting a run spike can be used if shown to meet the QA criteria.

7.5.1 Run Spike Procedure – Prepare both collection trains as per Section 6, choosing one as the spiked sample train and the other as the 'normal' sample train. Note that the spiked train will require a pre-spiked canister if analytes other than the ones shown in bold above are sampled. To leak check the collection trains (shown in Figure A3) disconnect one of the trains from the outlet of the heated filter box. Cap that connection and follow Section 6.5 to conduct the leak check procedure for the probe, filter box, and impinger/canister assembly for one train. For the disconnected impinger/canister train, follow Section 6.4 but disregard the probe and filter portion of the leak check procedure.

Follow Section 6.5 through Section 6.8 to complete a run spike making sure that both collection trains start simultaneously and operate in a similar manner.

After the start of the run, inject an aliquot of the aqueous spike solution (Section 5.15.1) into the first impinger of the spiked train. Note that the canister has already been pre-spiked if compounds not listed in bold above are analytes. The normal and spiked samples are separate samples whereby the spiked sample is collected, labeled, and analyzed separately from the normal sample.

7.5.1.1 Aqueous Field Spike – Prepare an aqueous field spike by injecting an aliquot (e.g., 1.0 mL) of aqueous spike solution into one of the sample bottles containing DI water and an [AQU] Internal Standard. The volume added must be equal to the volume used to spike the spiked sample train. Clearly label the aqueous field spike and analyze with the corresponding aqueous sample from the run spike.

7.5.1.2 Spiked Canisters and Gas Field Spike – Prior to going to the field, prepare one spiked canister for the spiked train sample run unless the analytes are limited to the list provided above in bold. A spiked canister is prepared by injecting an aliquot, for example 25 mL at ambient pressure, of the gas spike solution into a cleaned evacuated (<1.0 in Hga) canister. The gas spike solution can be transferred to the canister using a gas syringe with a valve. Use the same gas spike volume as injected into the spiked canisters prepared for the run spike. Clearly label this spike canister. This canister is used to establish the spike level for spike recovery purposes.

7.5.2 Notes Regarding Run Spikes – (1) Single run spikes should meet the equivalent spiking level criteria in Table 7.2. (2) Bracketed run spikes must meet the equivalent spiking level criteria in Table 7.3. (3) Each run spike must have an associated field spike. (4) The spiked and non-spiked (referred to as "normal") sample trains and associated samples should be separately labeled and named. (5) Like duplicates, trains must be isolated during leak checks. (6) Run spikes evaluate both accuracy and precision and, therefore, are typically more difficult than train spikes and duplicates.

Table 7.2 Single Run Spike Criteria for Equivalent Spiking Levels

If the *actual* source gas concentration of a targeted compound is…..	Then the equivalent spiking level for that targeted compound must be at or greater than the sample system detection limit and….
…less than 0.5 ppmvd	….. no more than 2 ppmvd
…between 0.5 to 1.5 ppmvd	….. no more than 6 ppmvd
…is greater than 1.5 ppmvd	….. no more than four times the source concentration

Table 7.3 Bracketed Run Spike Criteria for Equivalent Spiking Levels

Spiking Level	Criteria
Low Equivalent Spiking Level	Should be less than the actual source gas concentration. Must be no more than 5 times the actual source gas concentration, in order to be used in the spike recovery calculation.
High Equivalent Spiking Level	Must be less than or equal to 10 times the actual source gas concentration, in order to be used in the spike recovery calculation.

7.5.3 Equivalent Spiking Levels – All spikes introduced into the sample trains, either as a train spike (Section 7.6) or run spike (Section 7.5), have an "equivalent spiking level." This is defined as the compound concentration that would result if the spike were present in a dry standard gas of the same volume as the sample gas volume of the spiked sample trains as shown in Equation 7.2. For example, assume a spiked sample train operates at a dry standard flow rate of 500 mL per minute for one hour (30 liters, total) and a 1 mL spike is introduced that contains 100 mg/L (µg/mL) of methanol. 100 µg of methanol in 30 liters of gas yields an equivalent spiking level of 2.50 ppmvd of methanol. This is a theoretical, calculated concentration in air - not a measured concentration.

Equation 7.2

$$ESL_{ppmvd} = \frac{(\mu g\ Field\ Spike)(24.04)}{(L\ Sample Vol_{spiked\ train})(Cmpd.MW)}$$

Where:
ESL = Equivalent Spiking Level
µg Field Spike = µg of Compound in Field Spike
L Sample $Volume_{spiked\ train}$ = Liters of Sample Volume for Spiked Train
Cmpd. MW = Compound Molecular Weight

Ideally, the spike solution used for single run spikes would yield an equivalent spiking level that matches the source concentration for each compound. This, of course, is impossible. But, efforts should be made to match the equivalent spiking level to the source gas concentration. This method sets criteria for equivalent spiking levels for single run spikes and bracketed run spikes. Labs and/or sampling companies should estimate the source concentrations for every compound to be sampled at every source, and a spike solution should be formulated for each source that provides equivalent spiking levels near the source concentrations. Equivalent spiking levels that are very small relative to the source concentration make it very difficult to obtain good spike recoveries. Equivalent spiking levels that are very large relative to the source concentration make it easy to obtain a good spike recovery but do not necessarily demonstrate sampling proficiency. For this reason, NCASI has established criteria for equivalent spiking levels for this method. This method also allows bracketed spikes intended to help the user for cases in which the source concentration cannot be closely estimated.

The verification of an equivalent spiking level used for a particular sample event can only be accomplished after the run spike results have been compiled. For a run spike, the results provided by the non-spiked (or normal) impinger train will determine the *actual* source gas concentration for a targeted compound. The equivalent spiking level will be calculated using the results from analysis of the field spike and the gas sample volume of the spiked sample train. (The mass of compound in the field spike, determined from lab analysis, is used as the spiked mass for calculation of the equivalent spiking level.)

To check whether an equivalent spiking level meets the method criteria for a **single run spike**, select the appropriate concentration range in the left column of Table 7.2, then determine the maximum equivalent spiking level allowed for that concentration range as indicated in the right column of the table. The equivalent spiking level for a single run spike compound must be within the specified limits.

For **bracketed run spikes** the equivalent spiking level criteria are provided in Table 7.3. Bracketed run spikes are discussed in Section 7.5.6.

7.5.4 Run Spike Recovery Calculation – The percent recovery calculation for the aqueous spike and gaseous spike is shown in Figure A4. The calculation has three basic steps. (1) The gaseous concentration obtained from the normal sample train is subtracted from the concentration obtained from the spiked sample train. (2) The resulting concentration difference is then multiplied by the gaseous sample volume of the spiked sample train (with appropriate conversion factors) to obtain the mass of the spike that was recovered. (3) The mass recovered is divided by the mass spiked and expressed as a percent recovery, as shown in Equation 7.3. For compounds that are spiked into the canister (only), the mass recovered must be divided by the "canister mass correction factor" (see Section 9.1.3.3) before the percent recovery is calculated.

Equation 7.3

$$\%\,Recovery_{(i)} = \frac{mass_{recovered(i)}}{mass_{FS(i)}} \times 100$$

$mass_{\text{recovered}(i)}$ = mass of analyte (i) recovered by the spiked collection train
$mass_{\text{FS}(i)}$ = mass of analyte (i) in the aqueous and gas field spike

A spike recovery is not calculated for a targeted compound if the actual source gas concentration for that compound is measured below the detection limit (by the normal sample train).

Account for all laboratory and field dilutions in the computation of the mass.

7.5.4.1 Example Calculation – Assume the normal sample train and spiked sample train provide methanol concentrations of 2.5 and 5.5 ppmvd, respectively. Also, assume the spiked train had a dry standard sample volume of 30 liters and that 100 µg of methanol were spiked into the spiked train ($\text{mass}_{\text{field spike}}$) as determined from the aqueous field spike. The concentration difference between the two trains is 3.0 ppmvd. Multiplying the 3 ppmvd value by 30 liters and applying appropriate conversion factors yield a mass $\text{recovered}_{\text{spiked train}}$ of 120 µg of methanol. The final spike recovery is 120/100 x 100 = 120%. Note that the mass in the normal train cannot be subtracted from the mass of the spiked train (in

the first step) because the two sample trains do not typically have the same sample volumes.

7.5.5 Run Spike Recovery Criteria – The criteria for run spike recovery are provided in Table 7.4. If the user selects the single run spike option, the spike recovery results are directly compared to Table 7.4. If the user selects the bracketed run spike option, the user must calculate the run spike recovery according to the rules provided in Section 7.5.6.2 and compare the final result to Table 7.4.

Table 7.4. Spike Recovery Criteria

If the Actual Source Concentration is…..	Spike Recovery Range…..
….less than 0.5 ppmvd	…should be between 50 and 150%
…between 0.5 to 1.5 ppmvd	…should be between 60 and 140%
…greater than 1.5 ppmvd	…should be between 70 and 130%

7.5.6 Single Run Spike or Bracketed Run Spike Alternative – Users may want to use a single run spike if they are knowledgeable about source characteristics and reasonably confident of the source gas concentrations. The bracketed run spike alternative or option is provided for cases in which the source gas concentration is highly variable or otherwise difficult to estimate. The user chooses the procedure considered most appropriate on a source-by-source basis.

7.5.6.1 Low Level and High Level Bracketed Run Spikes – A low level run spike should be conducted at a low equivalent spiking level anticipated to be *below* the *expected* source gas concentration but above the detection limit for the targeted compound.

The high level run spike should be conducted at a high equivalent spiking level anticipated to be *above* the *expected* source gas concentration, but no more than 10 times the source gas concentration.

7.5.6.2 Bracketed Spike Recovery Calculation Rules – The following rules must be used for calculating the spike recovery for bracketed run spikes.

Rule 1. If the low equivalent spiking level is determined to be greater than 5 times the *actual* source gas concentration and the high equivalent spiking level is less than or equal to 10 times the *actual* source gas concentration for a targeted compound, then the *high* level run spike is used in determining the spike recovery.

Rule 2. If the low equivalent spiking level is equal to or less than 5 times the actual source gas concentration, and the high equivalent spiking level is greater than 10 times the *actual* source gas concentration for a targeted compound, then the *low* level run spike is used in determining the spike recovery.

Rule 3. If the low equivalent spiking level is less than or equal to 5 times the source concentration and the high equivalent spiking level is less than or equal to 10 times the *actual* source concentration for a targeted compound, then calculate the following four parameters:

(3a) The spike recovery of the low level run spike.

(3b) The percent difference in the low spike equivalent spiking level and the actual source gas concentration as shown in Equation 7.4.

Equation 7.4

$$LSPD = \frac{|LESL - C_A|}{C_A} x100$$

Where:

LSPD = low spike percent difference (absolute value)
LESL = low equivalent spiking level
C_A = actual source gas concentration

(3c) The spike recovery of the high level run spike.

(3d) The percent difference in the high spike equivalent spiking level and the actual source gas concentration as shown in Equation 7.5.

Equation 7.5

$$HSPD = \frac{|HESL - C_A|}{C_A} x100$$

Where:

HSPD = high spike percent difference (absolute value)
HESL = high equivalent spiking level
C_A = actual source gas concentration

The spike recovery for **Rule 3** is based on the following two options: (i) the average of the spike recoveries determined in 3(a) and 3(c) above **OR** (ii) the spike recovery corresponding to the smallest percent difference determined in 3(b) and 3(d) above. The user may pick the option that provides the better spike recovery value. If the average spike recovery option is used, the actual source gas concentration, for the purposes of evaluating the spike recovery criteria (Table 7.3), will be the average of the two normal sample trains.

Rule 4. If the low equivalent spiking level is determined to be more than 5 times the actual source gas concentration and the high equivalent spiking level is greater than 10 times the actual source gas concentration, the equivalent spiking levels do not meet the criteria in Table 7.3. In this case, a spike recovery calculation should not be conducted and a spike recovery should not be reported. The report, however, must state that the sampling company failed to meet the equivalent spiking level criteria.

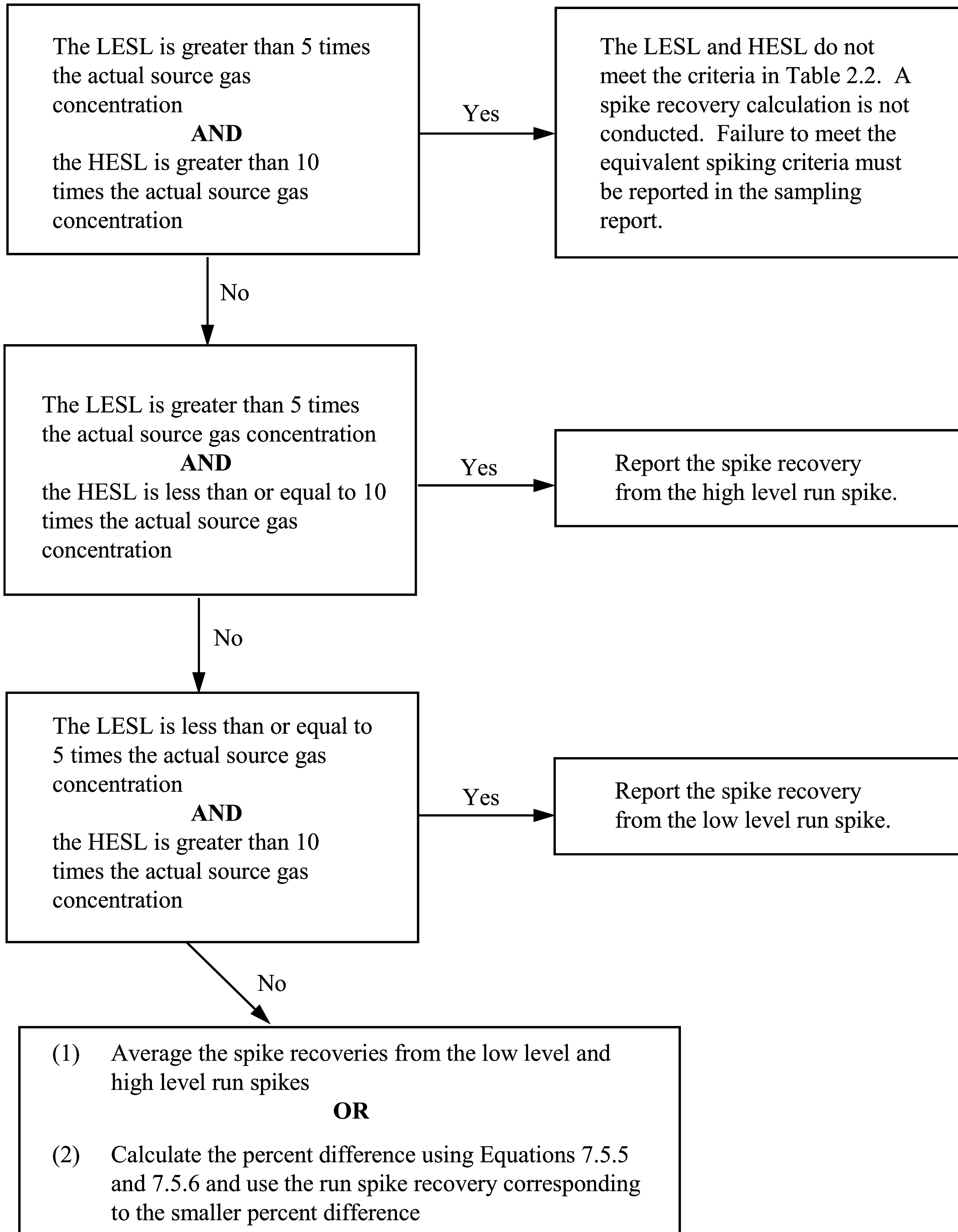
Figure 7.1 provides a flow diagram intended to help the user understand the bracketed spike recovery rules. Additionally, the appendix contains a worksheet and example calculation.

7.5.6.2.1 Example for a Bracketed Run Spike – A three run set on a source consisted of a duplicate, high run spike, and a low run spike. The *normal* sample train from both run spikes provided a source gas concentration of 10 ppmvd of methanol (considered the *actual* methanol concentration).

The low equivalent spiking level for the low run spike was 4 ppmvd. The spike recovery for the low run spike was 65%. Since 4 ppmvd equals or exceeds 40% of the *actual* source gas concentration, the low spike ratio was calculated to be 10/4 = 2.5.

The high equivalent spiking level was 30 ppmvd for the high run spike. The spike recovery for the high run spike was 90%. Since 30 ppmvd is less than 10 times the *actual* source gas concentration, the high spike ratio was calculated to be 30/10 = 3.

The bracketed run spike recovery for the source in this example could be based on either the (i) average of the low and high spike recoveries (77.5%) or (ii) the spiked sample train with the lower spike ratio, which provided a spike recovery of 65%. Assuming the sampling company chooses to use the 77.5% spike recovery, this value is assessed against the criteria in Table 7.4 and the sample set is shown to meet the spike recovery criteria.



HESL – high equivalent spiking level
LESL – low equivalent spiking level

Figure 7.1 Bracketed Spike Recovery Rules

7.5.7 Run Spike Reporting – Results of the run spike must be clearly calculated and reported for each analyte. A spike recovery should not be calculated if the source concentration is below detection limits. Spike recoveries must be clearly reported and sufficient data must be provided so that the results of the calculation are transparent.

7.6 Train Spike

The primary purpose of the train spike is to evaluate the entire sampling train's sampling accuracy and proficiency. (Note that the run spikes, which are spiked in the first impinger, do not evaluate the potential for compound loss in the probe and filter box.)

One spiked train sample run must be conducted for each mill visit. This QA procedure can be conducted prior to source testing, while in the field, or after source testing. However, this procedure must be conducted within 7 days of the first or last day of the mill sampling or mill visit.

Each compound evaluated by the train spike must be spiked at an equivalent spiking level above the detection limits but no more than 5 ppmvd.

If the analytes of interest are limited to acetaldehyde, acrolein, acetone, formaldehyde, methanol, phenol, methyl ethyl ketone, methyl isobutyl ketone, and propionaldehyde, the gas spike, gas field spike, and spiked canister discussed in this section are not needed.

The spiked train sample run will be conducted using only one collection train attached to the heated probe and filter box as shown in Figure A3. Use an unspiked evacuated canister. This collection train will be operated outside or independent of the source(s) tested. For the spiked train sample run, both an aqueous spike and a gas spike, if applicable, are injected into the probe tip of the collection train to determine the percent recovery of the spikes. Care must be taken to prevent introduction of any ambient organic contaminants during this procedure; activated charcoal tubes may be used for this purpose.

7.6.1 Train Spike Procedure – Prepare the collection train as per Sections 6.3 and 6.4, then follow Section 6.5 through Section 6.8 to complete the train spike. The sample flow rate and duration should be similar to the sample runs conducted at the mill or facility.

Note that two spikes will be injected into the probe tip of this collection train unless the analytes are limited to the list provided above in bold. After the start of the run, inject the gas spike first over a period of at least 5 minutes. Then follow with the injection of the aqueous spike over a period of at least 10 minutes. It is recommended that the aqueous spike be injected ***slowly*** into the heated probe tip over the duration of the remaining sample run. Prepare the aqueous and gas field spikes.

7.6.1.1 Aqueous Field Spike – Prepare an aqueous field spike by injecting an aliquot (e.g., 1.0 mL) of aqueous spike solution into one of the sample bottles containing DI water and an [AQU] Internal Standard. Clearly label the aqueous field spike and analyze with the corresponding aqueous sample from the run spike.

7.6.1.2 Spiked Canisters and Gas Field Spike – Prior to going to the field, prepare one spiked canister for the spiked train sample run unless the analytes are limited to the list provided above in bold. A spiked canister is prepared by injecting an aliquot, for example 25 mL at ambient pressure, of the gas spike solution into a cleaned evacuated (<1.0 in Hga) canister. The gas spike solution can be transferred to the canister using a gas syringe with a valve. Use the same gas spike volume as injected into the spiked canisters prepared for the run spike. Clearly label this spike canister.

The gas field spike will be injected into the probe tip of the collection train using a gas syringe with a valve. Use the same gas spike volume that was injected into the spiked canister.

7.6.2 Train Spike Notes – (1) Care must be taken to prevent introduction of any ambient organic contaminants during this procedure. Charcoal sorbent tubes placed at the probe tip to treat the ambient air entering the measurement system should minimize bias due to contamination. (2) Care should also be taken to inject the spike solution far enough into the heated probe to ensure complete volatilization of the aqueous spike. (3) The spike should be introduced over a 10 to 30 minute time period because a single quick injection may cause poor spike recovery. (4) The train spike must be operated for the same time period (usually one hour) and sample flow rate that is expected to be used during source sampling.

7.6.3 Train Spike QA Criteria – The percent recovery of the aqueous spiked compounds and the gaseous spiked compounds should each be 70% to 130%.

7.6.4 Train Spike Recovery Calculation – The percent spike recovery will be based on the mass recovered in the spiked train divided by the mass spiked (obtained from the field spikes). The method used to calculate the percent recovery is outlined in Figure A5 and shown in Equation 7.6. Account for all laboratory and field dilutions in the computation of the mass.

Equation 7.6

$$\%\,Recovery_{(i)} = \frac{mass_{ST(i)}}{mass_{FS(i)}} \times 100$$

$mass_{ST(i)}$ = mass of analyte (i) recovered by the spiked collection train
$mass_{FS(i)}$ = mass of analyte (i) in the aqueous and gas field spikes

Results of the train spike must be clearly calculated and reported for each analyte. Sufficient data must be presented such that the results are transparent.

8.0 Sample Analysis

Complete analysis of the impinger and canister samples will require four analytical techniques. If a select group of compounds is to be determined, then only use the analytical techniques that are required to obtain the desired concentrations in the aqueous and gas samples.

8.1 Sample Preparation

8.1.1 Aqueous Impinger Samples – Record the laboratory weight and verify the water level mark for each sample bottle prior to analysis. Note any differences. The sample bottles do not need to be at room temperature before weighing and must remain cold.

8.1.2 Gas Canister Samples – Record the pressure of each canister when delivered to the lab. If the canister samples require dilution, add nitrogen gas and record the final and initial pressure of the canister.

8.2 [AQU] GC/FID Analysis

Perform the analysis of the compounds of interest in the aqueous impinger samples by direct aqueous injection into a GC/FID.

8.2.1 [AQU] GC/FID Operating Parameters – Table A1 lists the recommended operating parameters for the GC/FID analysis of the aqueous samples. Other chromatographic columns and conditions may be used if it has been established that the compounds are adequately separated, quality control parameters are met, and no other interferences are present. Once the GC/FID system has been optimized for analytical separation and sensitivity, the operating conditions must remain constant for the analysis of all samples, blanks, calibration standards and quality assurance samples.

Optimal GC/FID operating conditions will produce distinct separate peaks for each analyte at established retention times. Verification of the GC/FID performance is recommended by running an analysis of a solution containing a high level [AQU] calibration standard and the [AQU] internal standard stock. Determine the retention time of each analyte relative to the internal standard. If using the recommended [AQU] internal standard stock solution (Section 5.6.1), place 10 μL into a 2.0 mL autosampler vial and fill the vial with a high concentration [AQU] calibration standard. The resulting concentration of the [AQU] internal standard in the autosampler vial will be 15 mg/L.

Compare the results with previously established retention times for the GC/FID instrument. If the retention times are significantly different, then adjust the [AQU] GC/FID operating parameters to return the retention times to the established values.

Troubleshooting tips: **The temperature of the samples in the autosampler must be kept at 4°C to inhibit the degradation of acrolein.** Some possible interfering compounds include ethanol, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. Also note that constant injections of aqueous samples can cause water to build up in the system. This will cause the retention times to shift and the peaks to broaden. It is recommended that after approximately 50 injections a bakeout of the system be performed. This should consist of heating the injector to 250°C, the oven to over 200°C, and the detector to 275°C for several hours.

8.2.2 [AQU] GC/FID Calibration Curves – The calibration curves will be based on the analysis of the [AQU] calibration standards prepared in Section 5.5. Obtain a 2.0 mL autosampler vial for each calibration standard and place 10 μL of the [AQU] internal standard stock (Section 5.6.1) into each vial. Then fill each vial with a different [AQU] calibration standard. The resulting concentration of the internal standard in the vials will be 15 mg/L.

Most analytical software will automatically generate calibration curves and verify the accuracy of each curve. Verification of a calibration curve shall be based on the determination of the relative standard deviation of the relative response factors obtained for each analyte of interest. Each point on a calibration curve will have a relative response factor (RRF_M). The RRF_M is calculated by Equation 8.1 using a relationship between the responses obtained for the internal standard and analyte.

Equation 8.1

$$RRF_M = \frac{A_M}{A_{IS}} x \frac{C_{IS}}{C_M}$$

RRF_M = Relative response factor for an analyte
A_M = area of analyte peak
A_{IS} = area of internal standard peak
C_M = concentration of analyte injected (mg/L)
C_{IS} = concentration of internal standard injected (mg/L)

A calibration curve will be acceptable when the relative standard deviation of the RRF_Ms are less than 20%. The average RRF_M will then be used to calculate the concentration of an analyte in an aqueous sample by Equation 8.2.

Equation 8.2

$$C_S = \frac{A_S \, x \, C_{IS}}{A_{IS} \, x \, average RRF_M}$$

C_S = Concentration of the analyte in the sample, mg/L
A_S = Area of the analyte peak in the sample
C_{IS} = Concentration of the internal standard, mg/L
A_{IS} = Area of the internal standard peak in the sample
average RRF_M = Relative response factor of analyte

If the calibration curve is not acceptable, then reanalyze the calibration solutions by developing another calibration curve and evaluating the relative standard deviation. If that evaluation also fails, then prepare new calibration standards and/or perform instrument maintenance.

8.2.3 [AQU] GC/FID QA Requirements – The GC/FID aqueous analytical technique includes both mandatory and recommended laboratory QA procedures. Laboratories must report the appropriate QA results along with the source sample results.

8.2.3.1 Laboratory Blank Sample - A laboratory blank sample must be analyzed prior to analysis. Additional laboratory blanks must be included for every 20 source samples analyzed. Blank samples are prepared from the DI water used to prepare the internal and calibration standards. Blank samples must include the appropriate internal standard.

8.2.3.2 Laboratory Duplicates – One laboratory duplicate of a source sample will be required. Additional laboratory duplicates will be required for every 10 source samples analyzed. Duplicates are a replicate injection

of the same source sample. Note that these samples already contain the internal standard.

The percent difference of the duplicate concentrations should be within 10%.

8.2.3.3 Calibration Verification Standard – The calibration verification standard shall be the mid-range [AQU] calibration standard. This calibration check must be performed prior to analysis, after every 10 source samples analyzed, and at the end of the analysis.
Compare the concentration reported by the instrument with the known concentration of the standard to verify instrument calibration. The percent recovery of the concentrations should be within 80% and 120%. If it is not, either prepare a new standard or perform instrument maintenance. If necessary, re-calibrate the instrument.

8.2.3.4 Second Source or Reference Standard – Analysis of a second source standard or a reference standard (Section 5.16) is required for each analyte following the initial analysis of the calibration verification standard. The second source or reference standard should match the results obtained for the calibration verification standard to demonstrate optimum analytical performance.

Compare the concentration of the second source or reference standard with the concentration of the calibration verification standard. The percent recovery of the concentrations should be within 70% and 130%. If it is not, either prepare a new standard or perform instrument maintenance. If necessary, re-calibrate the instrument.

8.2.3.5 Laboratory Matrix Spike Samples – A laboratory matrix spike sample may be prepared with each group of similar matrix type. Using the mean concentration determined by the replicate analyses, or the background level determined from a single measurement, determine the spiking level which will give one to four times the background. If the background sample does not have detectable levels of analytes, spike the sample at approximately five times the lowest calibration level of the instrument. Spike the sample with the determined amount of the calibration standard/matrix spike solution and proceed to analyze the sample in the normal manner. The calculated spike recovery should be 70 to 130%.

8.2.4 [AQU] GC/FID Source Sample Analysis – The concentration of the source samples must be determined from the calibration curves derived for the [AQU] GC/FID analytical technique. Note that the internal standard has already been added to the source samples.

8.3 [FOR] Acetylacetone Colorimetric Procedure

This analytical procedure will determine the concentration of formaldehyde in the aqueous samples. It is based on the ASTM Method D 6303-98. Note that this procedure does not require the use of an internal standard. Laboratories must report the appropriate QA results along with the source sample results.

8.3.1 Spectrophotometer Operating Parameters – The spectrophotometer must be capable of measuring absorbance at 412 nanometer wavelength.

8.3.2 [FOR] Calibration Curve – Prepare the six [FOR] Calibration Standards as described in Section 5.9. Add 2.0 mL of the acetylacetone reagent to each test tube and mix thoroughly. Place test tubes containing the calibration standards in the water bath for 10 minutes at 60^oC, then allow the test tubes to cool to room temperature.

The same spectrophotometer absorption cell will be used to analyze the six [FOR] calibration standards. The six concentrations will represent 0.0, 0.5, 1.0, 2.0, 5.0, and 7.5 mg/L formaldehyde, respectively. Follow the spectrophotometer manufacturer's instructions for calibrating the instrument by measuring the absorbance, at 412 nm, for each calibration standard.

The calibration curve should yield a linear plot of the absorbance value versus the corresponding formaldehyde concentration. The linear plot should have a correlation coefficient that is greater than 0.995. Determine the slope and y-intercept of the curve to develop a linear equation that must be used to determine the concentration of formaldehyde in the source samples.

Verification of the formaldehyde calibration curve is not required because the titration process to determine the formaldehyde content of the formalin solution, called for by the ASTM method, is a primary standard.

8.3.3 [FOR] Formaldehyde Laboratory QA Requirements – The formaldehyde analysis includes both mandatory and recommended laboratory QA procedures.

8.3.3.1 Laboratory Blank Sample - A laboratory blank sample must be analyzed prior to analysis. Additional laboratory blanks must be included for every 20 source samples analyzed. Blank samples are prepared from the DI water used to prepare the internal and calibration standards. Note that the blank samples for this analytical technique do not contain an internal standard.

8.3.3.2 Laboratory Duplicates – One laboratory duplicate of a source sample will be required. Additional laboratory duplicates will be required

for every 10 source samples analyzed. Duplicates are a replicate analysis of the same source sample.

The percent difference of the duplicate concentrations should be within 10%.

8.3.3.3 Calibration Verification Standard – The calibration verification standard shall be the mid-range [FOR] calibration standard. This calibration check must be performed prior to analysis, after every 10 source samples analyzed, and at the end of the analysis.

Compare the concentration reported by the instrument with the known concentration of the standard to verify instrument calibration. The percent recovery of the concentrations should be within 80% and 120%. If it is not, either prepare a new standard or perform instrument maintenance. If necessary, re-calibrate the instrument.

8.3.3.4 Second Source or Reference Standard – Analysis of a second source or reference standard (Section 5.15) is required following the initial analysis of the calibration verification standard. The second source or reference standard should match the results obtained for the calibration verification standard to demonstrate optimum analytical performance.

Compare the concentration of the second source or reference standard with the concentration of the calibration verification standard. The percent recovery of the concentrations should be within 70% and 130%. If it is not, either prepare a new standard or perform instrument maintenance. If necessary, re-calibrate the instrument.

8.3.4 [FOR] Formaldehyde Source Sample Analysis – Refer to the ASTM Method 06303-98 for complete details. In summary, remove a 2.0 mL aliquot of the impinger sample and transfer to a screw-capped test tube. Add 2.0 mL of the acetylacetone reagent and mix thoroughly. Place the test tube in a water bath for 10 minutes at 60°C. Allow test tubes to cool to room temperature. Transfer the cooled solution to an absorption cell and place in the spectrophotometer to measure the absorbance at 412 nm.

Use the absorbance value obtained for each source sample to calculate the formaldehyde concentration from the calibration curve developed by this procedure.

If the concentration of a sample is above 7.5 mg/L after the initial analysis, remove an aliquot of the original aqueous sample and dilute accordingly. Start the procedure over by using the diluted source sample. Confirm that this concentration is within the operating range of the instrument. Always dilute the

aliquot of the original source sample instead of diluting the colored (derivatized) solutions.

8.4 [MSD] GC/MSD Analysis

Perform the analysis of the canister samples by using a cryogenic preconcentrator to concentrate the sample for injection into a gas chromatograph followed by a mass selective detector. The delivery of the [MSD] Internal Standard should be automated by the preconcentrator. **The lab must insure that that pretreatment of the gas sample does not remove the polar compounds of interest.**

8.4.1 [MSD] GC/MSD Operating Parameters – Table A2 lists the recommended operating parameters for the preconcentrator and the GC/MSD instrument. Other chromatographic columns and conditions may be used if it has been established that the compounds are adequately separated, quality control parameters are met, and no other interferences are present. Once the [MSD] GC/MSD system has been optimized for analytical separation and sensitivity, the operating conditions must remain constant for the analysis of all samples, blanks, calibration standards and quality assurance samples.
Optimal [MSD] GC/MSD operating conditions will produce distinct separate peaks for each analyte at established retention times. Verification of the [MSD] GC/MSD performance is recommended by running an analysis of a solution containing a high level [MSD] Calibration Standard and the [MSD] Internal Standard. Determine the retention time of each analyte relative to the internal standard.

Compare the results with previously established retention times for the [MSD] GC/MSD instrument. If the retention times are significantly different, then adjust the [MSD] GC/MSD operating parameters to return the retention times to the established values.

8.4.2 [MSD] GC/MSD Calibration Curves – Develop a separate calibration curve for each compound being analyzed by the GC/MSD technique. The calibration curves will be based on the analysis of the [MSD] Calibration Standards prepared in Section 5.11. The delivery of the [MSD] Internal Standard should be automated by the preconcentrator for all samples and QA requirements. Most analytical software will automatically generate calibration curves and verify the accuracy of each curve.

Verification of a calibration curve shall be based on the determination of the relative standard deviation of the RRF_Ms obtained for each analyte of interest. Refer to Equation 8.2.2 (Section 8.2.2) to calculate the RRF_M for each calibration point along a calibration curve. A calibration curve will be acceptable when the relative standard deviation of the RRF_Ms are less than 20%. Use the average RRF_M to calculate the concentration of an analyte in a gas sample by Equation 8.2.

If the calibration curve is not acceptable, then reanalyze the calibration solutions by developing another calibration curve and evaluating the relative standard deviation. If that evaluation also fails, then prepare new calibration standards and/or perform instrument maintenance.

8.4.3 [MSD] GC/MSD QA Requirements – The GC/MSD technique includes both mandatory and recommended laboratory QA procedures. Laboratories must report the appropriate QA results along with the source sample results.

8.4.3.1 Laboratory Blank Sample - A laboratory blank sample must be analyzed prior to analysis. Additional laboratory blanks must be included for every 20 source samples analyzed. Blank samples are prepared from the nitrogen gas used to prepare the calibration standards.

8.4.3.2 Laboratory Duplicates – One laboratory duplicate of a source sample will be required. Additional laboratory duplicates will be required for every 10 source samples analyzed. Duplicates are a replicate injection of the same source sample.

The percent difference of the duplicate concentrations should be within 10% (Section 6.9.2.2).

8.4.3.3 Calibration Verification Standard – The calibration verification standard shall be the appropriate mid-range [MSD] calibration standard.

This calibration check must be performed prior to analysis, after every 10 source samples analyzed, and at the end of the analysis.

Compare the concentration reported by the instrument with the known concentration of the standard to verify instrument calibration. The percent recovery of the concentrations should be within 80% and 120%. If it is not, either prepare a new standard or perform instrument maintenance. If necessary, re-calibrate the instrument.

8.4.3.4 Second Source or Reference Standard – Analysis of a second source or reference standard (Section 5.16) is required for each analyte following the initial analysis of the calibration verification standard. The second source or reference standard should match the results obtained for the calibration verification standard to demonstrate optimum analytical performance.

Compare the concentration of the second source or reference standard with the concentration of the calibration verification standard. The percent recovery of the concentrations should be within 70% and 130%. If it is

not, either prepare a new standard or perform instrument maintenance. If necessary, re-calibrate the instrument.

8.4.3.5 Laboratory Matrix Spike Samples - A laboratory matrix spike sample may be prepared with each group of similar matrix type. Using the mean concentration determined by the replicate analyses, or the background level determined from a single measurement, determine the spiking level which will give one to four times the background. If the background sample does not have detectable levels of analytes, spike the sample at approximately five times the lowest calibration level of the instrument. Spike the sample with the determined amount of the calibration standard/matrix spike solution and proceed to analyze the sample in the normal manner. The calculated spike recovery should be 70 to 130%.

8.4.4 [MSD] GC/MSD Source Sample Analysis

8.4.4.1 Record the temperature and pressure of each canister at laboratory conditions.

8.4.4.2 If dilution of a canister sample is required for analysis, then fill the appropriate canisters to 40 in Hga or above with nitrogen gas. Record the final pressure and temperature of each diluted canister.

8.4.4.3 Using a preconcentrator, inject a sample from each canister into the GC/MSD. The concentration of the samples analyzed must be determined from the calibration curves developed for this procedure.

8.5 [TER] GC/FID Analysis

Perform the analysis of the terpene compounds collected in the canister by using a gas sample loop to introduce the gas sample into the GC/FID. Note that there is no internal standard for terpene analysis.

8.5.1 [TER] GC/FID Operating Parameters – Table A3 lists the recommended operating parameters for the GC/FID analysis for terpene compounds. Other chromatographic columns and conditions may be used if it has been established that the compounds are adequately separated, quality control parameters are met, and no other interferences are present. Once the [TER] GC/FID system has been optimized for analytical separation and sensitivity, the operating conditions must remain constant for the analysis of all samples, blanks, calibration standards and quality assurance samples.

Optimal [TER] GC/FID operating conditions will produce distinct separate peaks for each analyte at established retention times. Verification of the [TER] GC/FID performance is recommended by running an analysis of a solution containing a

high level [TER] calibration standard. Determine the retention time of each terpene compound. Note that there is no internal standard used in the terpene analysis.

Compare the results with previously established retention times for the [TER] GC/FID instrument. If the retention times are significantly different, then adjust the [TER] GC/FID operating parameters to return the retention times to the established values.

8.5.2 [TER] GC/FID Calibration Curves – Develop a separate calibration curve for each compound being analyzed by the [TER] GC/FID technique. The calibration curves will be based on the analysis of the [TER] calibration standards prepared in Section 5.14. Most analytical software will automatically generate the calibration curves and verify the accuracy of each curve.

Verification of a calibration curve shall be based on the linear plot of the terpene concentration versus corresponding GC/FID area count. Calibration will be acceptable if the correlation coefficient for the curve is greater than 0.995. Determine the slope and y-intercept of the curve to develop a linear equation that must be used to determine the concentration of terpenes in the source samples.

If the calibration curve is not acceptable, then reanalyze the calibration gas mixtures by developing another calibration curve and evaluating the correlation coefficient. If that evaluation also fails, then prepare new calibration standards and/or perform instrument maintenance.

8.5.3 [TER] GC/FID QA Requirements – The [TER] GC/FID procedure includes both mandatory and recommended laboratory QA procedures. Laboratories must report the appropriate QA results along with the source sample results.

8.5.3.1 Laboratory Blank Sample – A laboratory blank sample must be analyzed prior to analysis. Additional laboratory blanks must be included for every 20 source samples analyzed. Blank samples are prepared from the nitrogen gas used to prepare the calibration standards.

8.5.3.2 Laboratory Duplicates – One laboratory duplicate of a source sample will be required. Additional laboratory duplicates will be required for every 10 source samples analyzed. Duplicates are a replicate injection of the same source sample.

The percent difference of the duplicate concentrations should be within 10% (Section 6.9.2.2).

8.5.3.3 Calibration Verification Standard – The calibration verification standard shall be the appropriate mid-range [TER] calibration

standard. This calibration check must be performed prior to analysis, after every 10 source samples analyzed, and at the end of the analysis.

Compare the concentration reported by the instrument with the known concentration of the standard to verify instrument calibration. The percent recovery of the concentrations should be within 80% and 120%. If it is not, either prepare a new standard or perform instrument maintenance. If necessary, re-calibrate the instrument.

8.5.4 [TER] GC/FID Source Sample Analysis – Obtain a gas sample from each canister and analyze using the GC/FID. The concentration of the samples analyzed must be determined from the calibration curves developed for this procedure.

8.5.4.1 Record the temperature and pressure of each canister at laboratory conditions.

8.5.4.2 If dilution of a canister sample is required for analysis, then fill the appropriate canisters to 40 in Hga or above with nitrogen gas. Record the final pressure and temperature of each diluted canister.

8.5.4.3 Inject a sample from each canister into the GC/FID. The concentration of the samples analyzed must be determined from the calibration curves developed for this procedure.

9.0 Calculations

The stack gas concentration of each analyte will be determined by combining the data collected from the sample train and laboratory analyses. The following calculation procedure has been provided as guidance. Other calculation methods may be used if shown to be valid.

This method has been developed to determine the emission source gas concentration of the compounds listed in Table 2.1. Some of these compounds will be captured in the aqueous impinger sample, some will be collected in both the aqueous and canister sample, and the rest will be collected in the canister. The calculations provided determine the mass of each compound captured in the impinger and canister samples and the corresponding source gas concentration.

9.1 Total Mass Captured by the Collection Train

The total mass of a compound is determined by combining the mass captured in the aqueous sample with the corrected mass captured in the canister sample. The procedure used to calculate the total mass can also be used to determine the mass for the percent recovery calculations required by the QA procedures in this method.

9.1.1 Mass Collected in the Aqueous Sample – The mass of an analyte in the aqueous sample is determined by multiplying the aqueous concentration of the analyte by the volume of the aqueous sample.

9.1.1.1 Mass of Formaldehyde – The formaldehyde concentration is determined by a different analytical procedure than the other compounds of interest in the aqueous sample. Therefore, the mass of formaldehyde in Equation 9.1 is calculated using the final volume of the aqueous sample obtained by the collection train (sample plus rinse).

Equation 9.1

$$mass_{HCOH,\ aqueous} = C_{HCOH} \text{ x } V_{f,aqueous}$$

$mass_{HCOH,aqueous}$ = mass of formaldehyde in the aqueous sample, µg
C_{HCOH} = concentration of formaldehyde in aqueous sample, µg/mL
$V_{f,aqueous}$ = final volume of aqueous sample, mL

9.1.1.2 Mass of [AQU] Compounds – The determination of the mass for the remaining compounds in the aqueous sample is based on a fixed sample volume, 100 mL, and the concentration (Equation 9.2).

Equation 9.2

$$mass_{[AQU],aqueous} = C_{[AQU]} \ x\ 100\ mL$$

$mass_{[AQU],aqueous}$ = mass of [AQU] analyte in the aqueous sample, µg
$C_{[AQU]}$ = concentration of analyte$_i$ in the aqueous sample, µg/mL

The final volume of the [AQU] samples are fixed at 100 mL because both the [AQU] internal standard and the [AQU] primary stock solution were prepared in 100 mL.

9.1.2 Mass Collected in the Canister – The collection train only captures a slip-stream of the source gas in the canister, while the total sample of the source gas passes through the impingers. Because of this, the resulting mass collected in the canister will have to be adjusted by a correction factor.

First, however, the mass of each compound captured in the canister is determined by multiplying the volume of the sample gas at standard conditions by the concentration as determined by the [MSD] GC/MSD or [TER] GC/FID analytical procedures. Note that the dry concentration in the canister will only be equivalent to the dry concentration in the source gas for those compounds that are not partially captured in the aqueous sample and for canister samples that have not been diluted prior to laboratory analysis.

9.1.2.1 Volume of Gas Sample in Canister – The interior volume of the canister used in this method is 6.0 liters. Equation 9.3 calculates the volume of the gas sample in the canister at standard conditions.

Equation 9.3

$$V_{GS,\,std} = 6.0\,L\left(\frac{528°R}{T_{GS}}\right)\left(\frac{P_{GS}}{29.92\text{ in Hg}}\right)$$

$V_{GS,\,std}$ = wet standard volume of gas sample at standard conditions, wsL
T_{GS} = temperature of gas sample (equivalent to canister temperature) at laboratory conditions, °R
P_{GS} = pressure of the gas sample prior to analysis, in Hga

9.1.2.2 Mass of [MSD] or [TER] Compounds in Canister Sample – Obtain the concentration of the compounds of interest in the canister gas sample by the [MSD] GC/MSD or [TER] GC/FID analytical procedures. Then combine the concentration with the standard sample gas volume to calculate the mass of analyte$_{(i)}$ in the canister using Equation 9.4.

Equation 9.4

$$mass_{i,\,canister} = \left(\frac{C_{i,\,[MSD]\;or\;[TER]}}{10^9}\right)\left(V_{GS,std}\right)\left(\frac{1\,gmole}{24.055\,L}\right)\left(MW_{(i)}\right)\left(\frac{10^6\,mg}{g}\right)$$

$mass_{i,canister}$ = mass of analyte$_{(i)}$ in the canister, µg
$C_{i,\,[MSD]\text{ or }[TER]}$ = concentration of [MSD] or [TER] analyte in wet canister sample gas, ppbvw
$V_{GS,std}$ = wet standard volume of gas sample at standard conditions, wsL (one atmosphere and 68°F)
$MW_{(i)}$ = molecular weight of analyte$_i$, g/gmole

9.1.3 Canister Mass Correction Factor – A mass correction factor is used to adjust the mass collected in the canister. This correction factor is based on the ratio of the total dry volume of source gas sampled through the collection train to the dry volume of the sample collected in the canister at the end of the sample run.

9.1.3.1 Total Dry Volume of Source Gas Sampled – This method assumes that the flow rate of the collection train is measured at the probe tip using a soap-bubble meter. The ambient air entering the bubble meter, however, becomes saturated from passing over the surface of the liquid reservoir. Therefore, the flow will have to be corrected to dry conditions, assuming saturated conditions using the vapor pressure of water at the

ambient temperature. Calculate the dry standard flow rate measured prior to and after the sample run using Equation 9.5.

Equation 9.5

$$Q_{probe,drystd} = Q_{probe,meas}\left(\frac{P_{bar} - P_{vap}}{29.92\, in\, Hg}\right)\left(\frac{528^{o} R}{T_{meas}}\right)$$

$Q_{probe,\ drystd}$ = dry standard flow rate measured at the probe tip of the sample collection train, dsL/min
$Q_{probe,\ meas}$ = actual flow rate measured at the probe tip of the sample collection train, L/min
P_{bar} = barometric pressure at flow rate measurement site, in Hga
P_{vap} = water vapor pressure in the gas stream being measured, assumed to be saturated at ambient dry temperature, in Hga.
T_{meas} = ambient temperature at flow rate measurement site, °R

Then, calculate the total volume of source gas sampled by multiplying the average flow rate of the collection train by the duration of the sample run using Equation 9.6.

Equation 9.6

$$V_{sourcegas,drystd} = \left(\frac{Q_{(i)\,probe,drystd} + Q_{(f)\,probe,drystd}}{2}\right) \times t$$

$V_{sourcegas,drystd}$ = total dry standard volume of source gas sampled by the collection train, dsL
$Q_{(i)probe,drystd}$ = pre-sample run dry standard flow rate measured at the probe tip of the sample collection train, dsL/min
$Q_{(f)probe,drystd}$ = post-sample run dry standard flow rate measured at the probe tip of the sample collection train, dsL/min
t = duration of sample run, minutes

9.1.3.2 Dry Volume of Canister Sample Collected – This parameter represents the volume of the gas sample collected at the end of the sample run. Determine the volume of gas present in the canister at the start and end of the of the sample run using Equations 9.7 and 9.8. It is assumed that no moisture is present in the evacuated canisters.

Equation 9.7

$$V_{(o)canistergas,drystd} = 6.0L \times \left(\frac{P_{o,can}}{29.92\, in\, Hg} \right) \left(\frac{528^{o}R}{T_{o,can}} \right)$$

$V_{(o)canistergas,drystd}$ = dry standard canister gas volume, dsL, at start of sample run
$P_{o,can}$ = pressure of the canister, in Hga, at start of sample run
$T_{o,can}$ = temperature of canister gas sample, °R, at start of sample run

Equation 9.8

$$V_{(f)canistergas,drystd} = 6.0L \times \left(\frac{P_{f,can} - P_{vap@38^{o}F}}{29.92\, in\, Hg} \right) \left(\frac{528^{o}R}{T_{f,can}} \right)$$

$V_{(f)canistergas,\ drystd}$ = dry standard canister gas volume, dsL, at the end of the sample run
$P_{(f)can}$ = measured pressure of the canister, in Hga, at the end of the sample run
$P_{vap@38°F}$ = moisture correction for water vapor in canister equivalent to 0.2292 in Hga; gas stream assumed saturated leaving the impinger train at 38°F
$T_{(f)can}$ = temperature of canister gas sample, °R, at the end of the sample run

Then calculate the difference in the pre- and post- canister volumes using Equation 9.9.

Equation 9.9

$$V_{canistersample,drystd} = V_{(f)canistergas,drystd} - V_{(o)canistergas,drystd}$$

$V_{canistersample,drystd}$ = dry standard volume of canister sample collected, dsL
$V_{(f)canistergas,drystd}$ = dry standard canister gas volume at the end of the sample run, dsL
$V_{(o)canistergas,drystd}$ = dry standard canister gas volume at the start of the sample run, dsL

9.1.3.3 Canister Mass Correction Factor – Since the volume of source gas sampled through the probe tip of the collection train is greater than the sample volume sent to the canister, the resulting mass of each analyte detected in the canister has to be corrected. This mass correction factor is calculated by Equation 9.10.

Equation 9.10

$$CF = \frac{V_{sourcegas,drystd}}{V_{canistersample,drystd}}$$

CF = canister mass correction factor
$V_{sourcegas,drystd}$ = total dry standard volume of source gas sampled by the collection train, dsL
$V_{canistersample,drystd}$ = dry standard volume of canister sample collected, dsL

9.1.4 Total Mass Captured by the Collection Train – The mass of the compounds collected in the aqueous sample will be combined with the corrected mass collected in the canister sample using Equation 9.11.

Equation 9.11

$$mass_{i,total} = mass_{i,aqueous} + (mass_{i,canister}\ x\ CF)$$

$mass_{i,total}$ = total mass of $analyte_{(i)}$ captured by the collection train, µg
$mass_{i,aqueous}$ = mass of $analyte_{(i)}$ in the aqueous sample, µg
$mass_{i,canister}$ = mass of $analyte_{(i)}$ in the canister sample, µg
CF = canister mass correction factor

9.2 Concentration in the Source Gas Sample – The source gas concentration for each compound of interest can be determined by converting the total mass captured into a dry gas volume equivalent of the pure compound and then dividing by the total dry volume sampled by the collection train, as shown by Equation 9.12.

9.2.1 Equation 9.12

$$C_{i,source\ gas} = \frac{mass_{i,total} \times \left(\frac{g}{10^6\ mg}\right)\left(\frac{1}{MW_i}\right)\left(\frac{24.055L}{gmole}\right)\left(\frac{10^6\ mL}{L}\right)}{V_{sourcegas,drystd}}$$

$C_{i,sourcegas}$ = concentration of $analyte_{(i)}$ in the source gas, ppmvd
$mass_{i,total}$ = total mass of $analyte_{(i)}$ captured by the collection train, µg
$MW_{(i)}$ = molecular weight of $analyte_i$, g/gmole
$V_{sourcegas,drystd}$ = total dry standard volume of source gas sampled by the collection train, dsL

Appendix

APPENDIX

Table A1 Recommended Operating Conditions for the [AQU] GC/FID Analysis of the Impinger Samples A1

Table A2 Recommended Operating Conditions for the Preconcentrator and [MSD] GC/MS Analysis of the Canister Samples A2

Table A3 Recommended Operating Conditions for the [TER] GC/FID Analysis of the Canister Samples A3

Figure A1 Schematic of Sample Analyses and Analytes A4

Figure A2 Chilled Impinger/Canister Sample Collection Trains A5

Figure A3 Quality Assurance Sample Collection Trains A6

Figure A4 Percent Recovery for the Run Spike A7

Figure A5 Percent Recovery for the Train Spike A8

Example Field Data Collection Sheet A9

Bracketed Spike Recovery Example A10

Worksheet for Determining the Spike Recovery QA Procedure for IM/CAN/WP-99.02 ..... A11

Summary of Quality Assurance Procedures A14

Table A1. Recommended Operating Conditions for the [AQU] GC/FID Analysis of the Impinger Samples

Injection:	Direct (Splitless)
Injector Temperature:	110°C
Injection Volume:	1 μL
Injection Liner Size:	2 mm id (no packing)
Syringe Rinse	10 rinses with VOC free DI water
FID Detector Temperature:	275°C
H_2 Flow Rate:	Approx. 50 mL/min
Air Flow Rate:	Approx. 500 mL/min
Makeup Gas:	Helium
Makeup Gas Flow Rate:	Approx. 25 mL/min
Carrier Gas:	Helium
Carrier Gas Flow Rate:	Constant pressure mode to give 6 mL/min at room temperature
Column:	J&W DB-624, 60 m (or longer) x 0.53 mm id x 3 micron fused silica capillary column with 10 m deactivated fused silica guard column
Cryogenics:	On
Temperature Program °C:	
Initial:	0°C for 3 min
Ramp 1:	5°C/min to 50°C for 0 minutes
Ramp 2:	70°C/min to 105°C for 17 minutes
Ramp 3:	70°C/min to 220°C for 3 minutes
Retention Time Order:	Acetaldehyde, Methanol, Acrolein, Propionaldehyde, Methyl Ethyl Ketone, Methyl Isobutyl Ketone, Cyclohexanol, Phenol

Table A2. Recommended Operating Conditions for the Preconcentrator and [MSD] GC/MS Analysis of the Canister Samples

Cryogenic Preconcentrator	
Sample Volume for Calibration:	500 mL
Module 1 Trap Temperature:	-150°C
Module 1 Desorb Temperature:	20°C
Module 2 Trap Temperature:	-10°C
Module 2 Desorb Temperature:	180°C
Module 3 Trap Temperature:	-170°C
Module 3 Inject Temperature:	100°C
Transfer Line Temperature:	100°C
Gas Chromatograph/Mass Selective Detector	
Inlet Temperature:	180°C
Carrier Gas:	Helium
Carrier Gas Flow Rate:	Constant flow mode at 2.0 mL/min
Column:	J&W DB-624, 60 m x 0.25 mm id x 1.4 micron fused silica capillary column with 10 m deactivated fused silica guard column
Cryogenics:	On
Temperature Program °C:	
Initial:	20°C for 3 min
Ramp 1:	3°C/min to 100°C for 3 minutes
Ramp 2:	5°C/min to 140°C for 2 minutes
Ramp 3:	7°C/min to 240°C for 0 minutes
Total Run Time:	57 min
Mass Range Scan:	29-250 amu

Table A3. Recommended Operating Conditions for the [TER] GC/FID Analysis of the Canister Samples

Parameter	Condition
Injection:	Split
Injector Temperature:	180°C
Injection Volume:	2 mL – sample loop
Split Ratio:	1.5:1
Split Flow:	4.8 mL/min
Total Flow:	9.8 mL/min
FID Detector Temperature:	250°C
H_2 Flow Rate:	40 mL/min
Air Flow Rate:	450 mL/min
Makeup Gas:	Helium
Makeup Gas Flow Rate:	45 mL/min
Carrier Gas:	Helium
Carrier Gas Flow Rate:	Ramped pressure mode. Initial pressure 14.0 psi. Ramp 7 psi/min to 9.3. Initial flow 3.2 mL/min.
Column:	J&W DB-1, 30 m x 0.32 mm id x 0.25 micron fused silica capillary column with 10 m deactivated fused silica guard column
Cryogenics:	Off
Temperature Program °C:	
Initial:	55°C for 16 min
Ramp 1:	120°C/min to 240°C for 2 minutes
Retention Time Order:	Cumene, α-pinene, camphene, β-pinene, p-mentha-1,5-diene, 3-carene, p-cymene, limonene

Figure A1. Schematic of Sample Analyses and Analytes

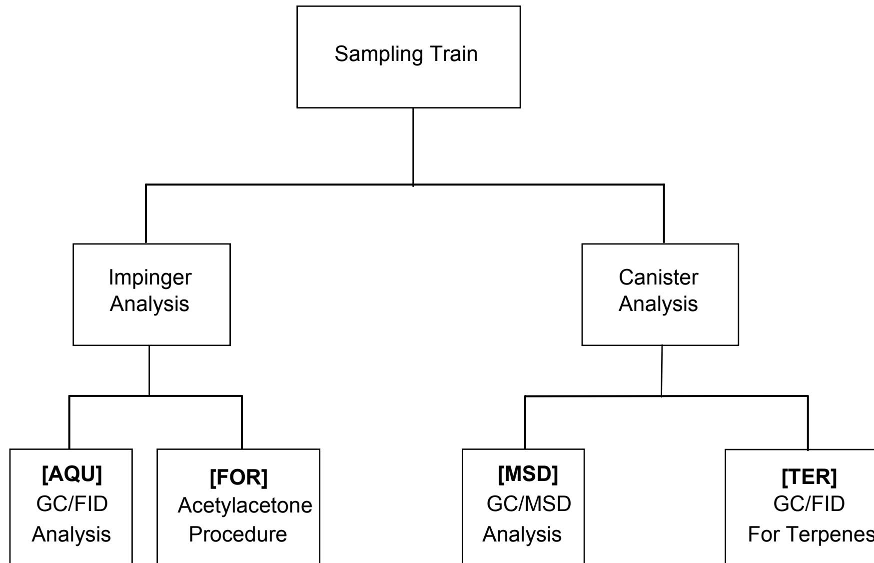


Figure A2. Chilled Impinger/Canister Sample Collection Trains

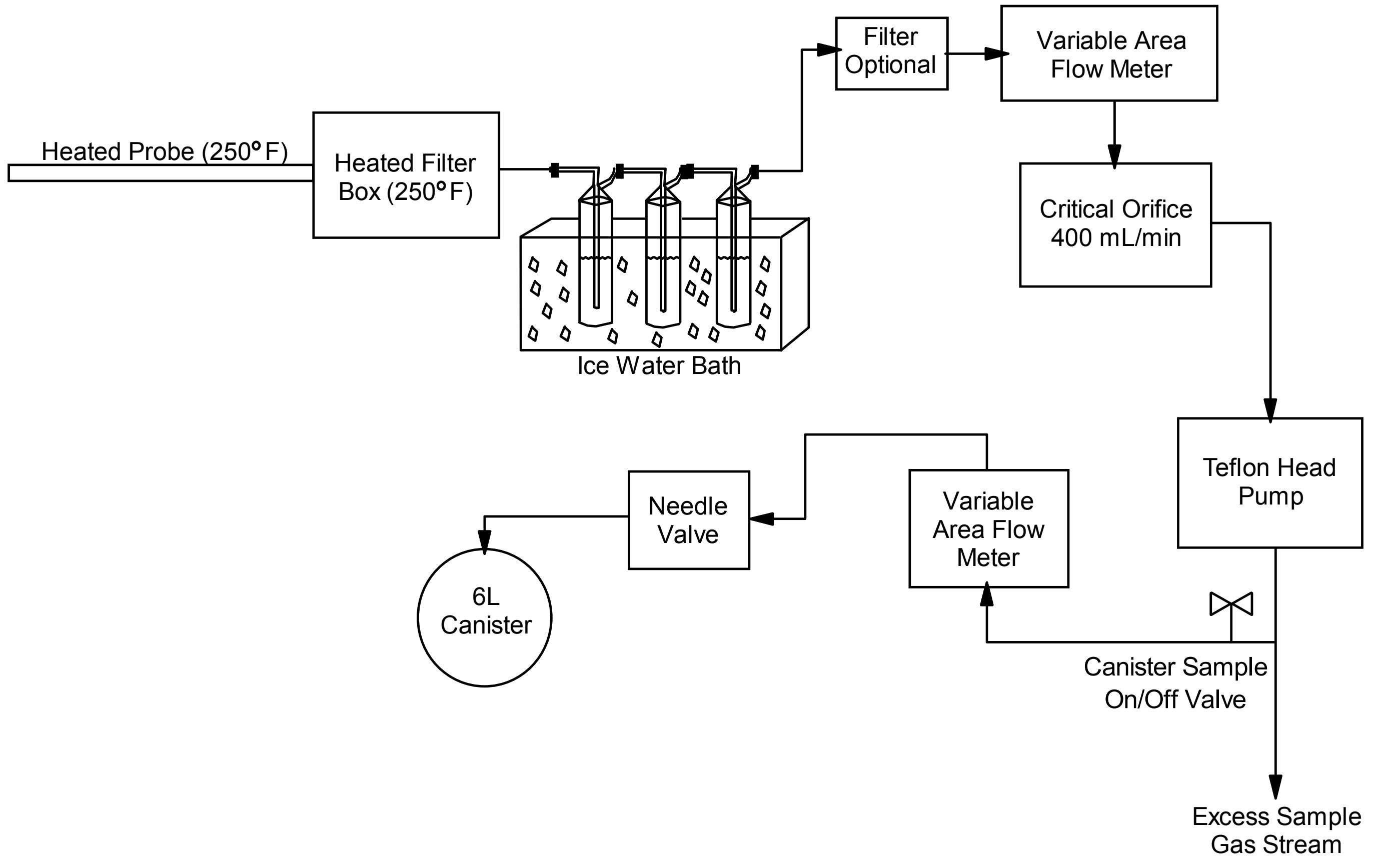


Figure A3. Quality Assurance Sample Collection Trains

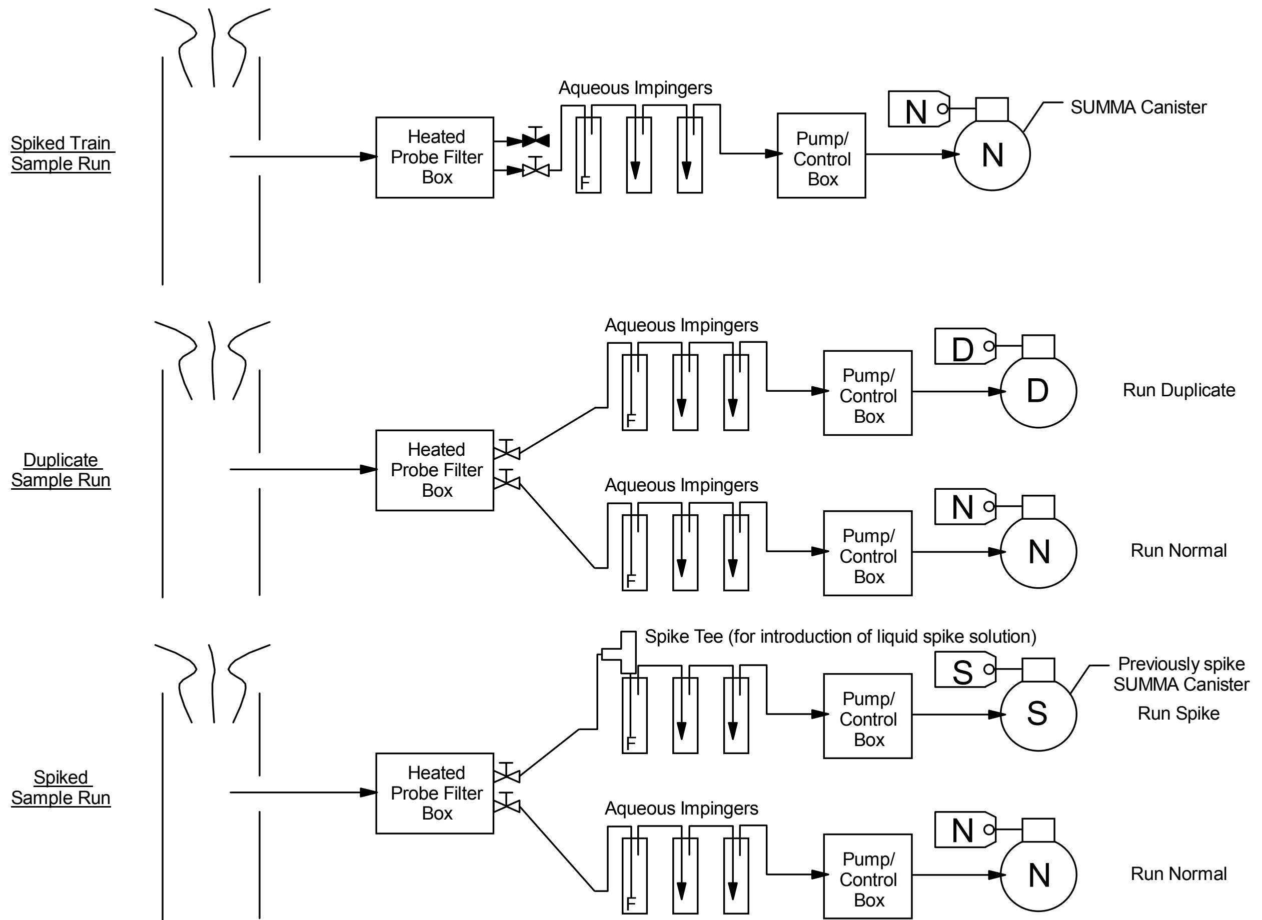


Figure A4. Percent Recovery for the Run Spike

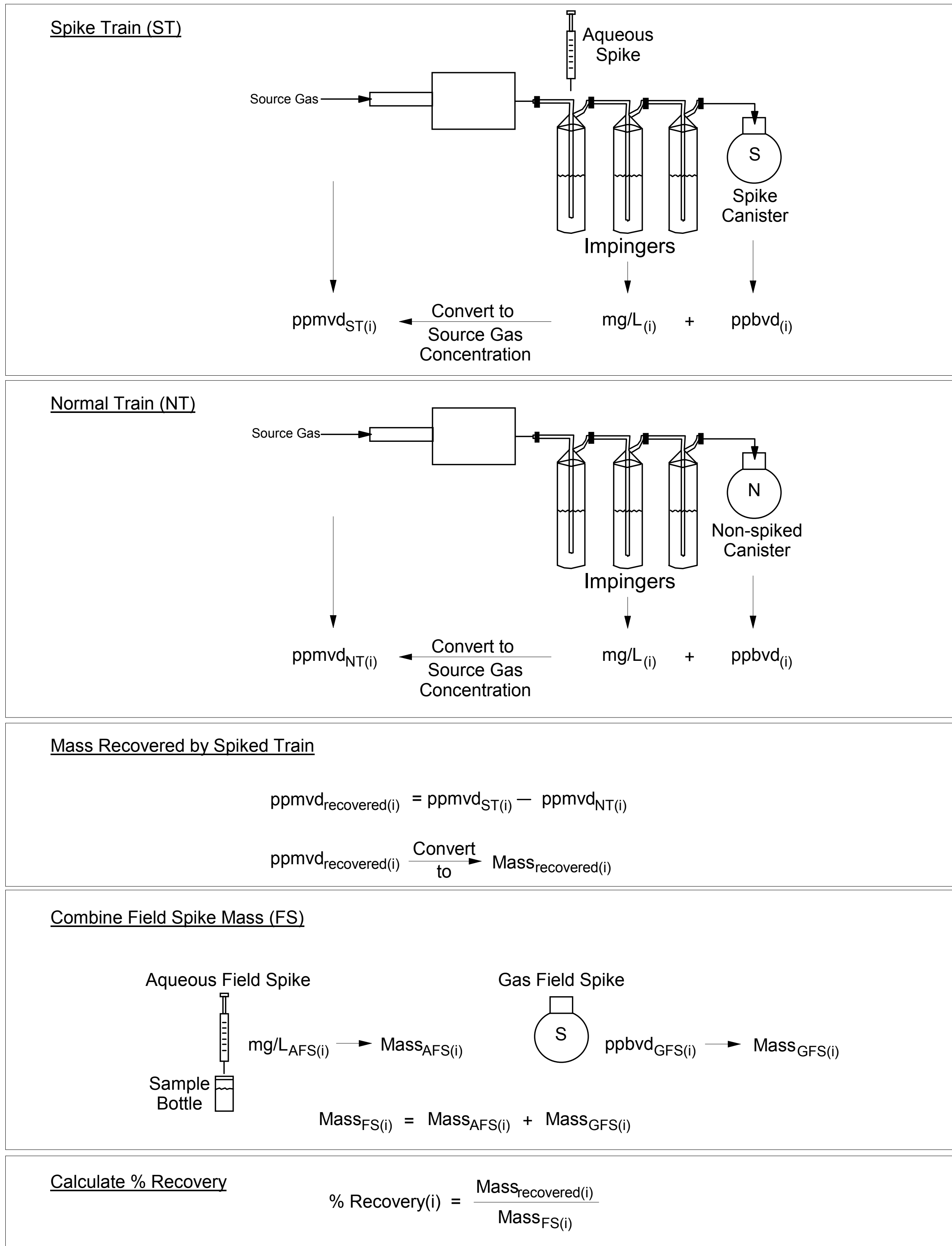
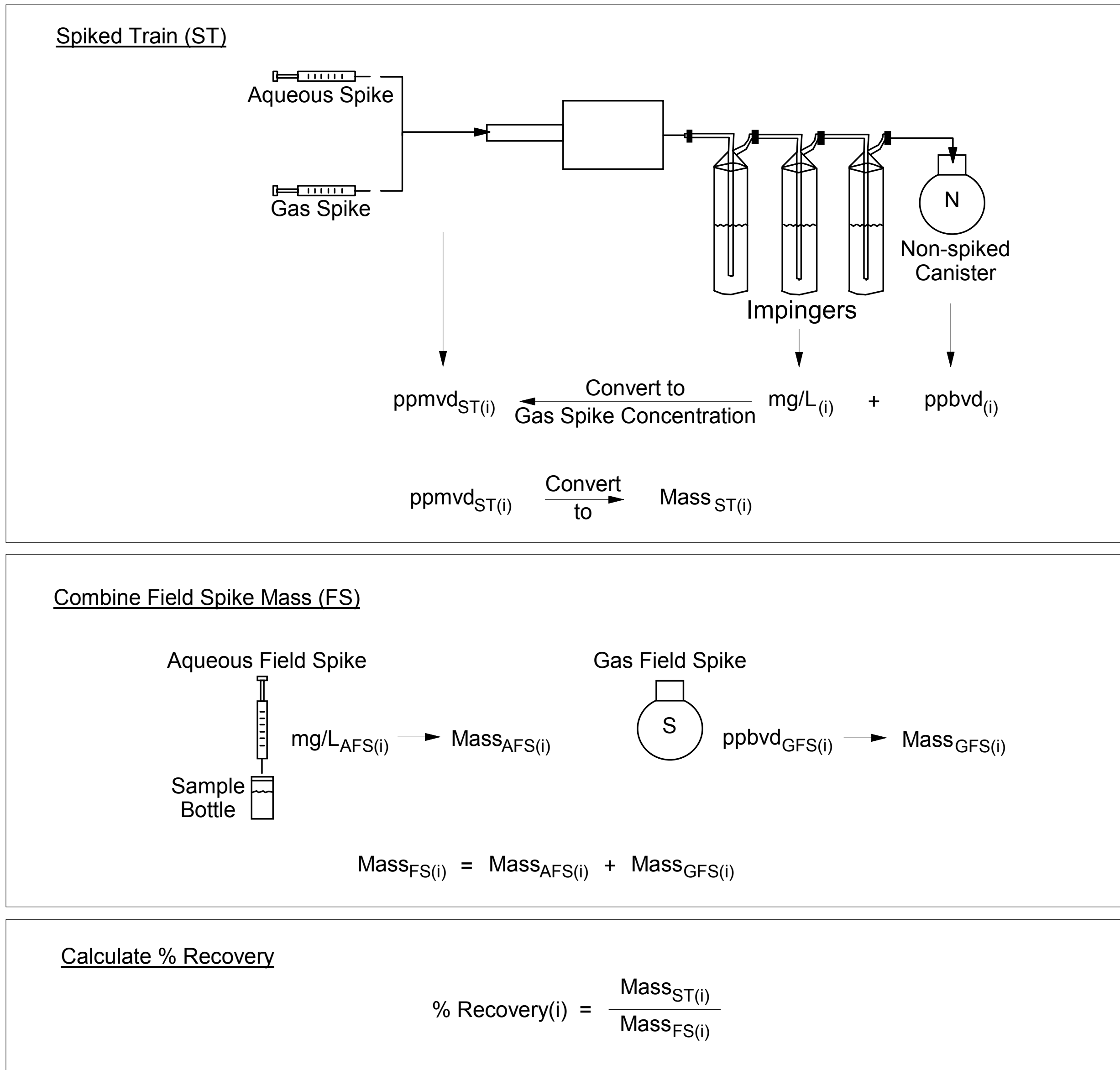


Figure A5. Percent Recovery for the Train Spike



EXAMPLE FIELD DATA COLLECTION SHEET

NCASI HAPS TRAIN FIELD DATA SHEET

SAMPLER	DATE:	CANISTER ID#	CAN CODE:	TRAIN SPIKE
SAMPLING CODE:			FIELD SPKIE Y N	gas____mL aqueous_____mL
DESCRIPTION:				

	PRESSURE	SECTION 1a	SECTION 1b	SECTION 2	SECTION 3	SECTION 4	SECTION 5
LEAK	INITIAL						
CHECK	FINAL						
	DIFFERENCE						

	PROBE SAMPLE FLOW RATES		COMBINED TRAIN FLOW RATES	
	PRE-RUN	POST-RUN	PRE-RUN	POST-RUN
1				
2				
3				
4				
5				
AVG				
% DIFFERENCE			% DIFFERENCE	

AMBIENT TEMPERATURE / PRESSURE			
PRE-RUN		POST-RUN	
°F	in. Hga	°F	in. Hga

	IMPINGER		LEFT VAC. GA.	CANISTER				VENT
	TIME	FLOW (mL/min)	(in. Hga)	TIME	P (in Hga)	FLOW (mL/min)	TEMP °F	FLOW (mL/min)
START								
5								
10								
15								
20								
25								
30								
35								
40								
45								
50								
55								
STOP								

COMMENTS:

Example: Bracketed Spike Recovery

compound	acrolein	acetaldehyde	formaldehyde	methanol	propionaldehyde	phenol
molecular weight	56.06	44.05	30.05	32.04	58.08	94.11
Low Level Run Spike (Low Level Spiked Sample Train)						
normal sample train sample volume (L)	30	30	30	30	30	30
spiked sample train sample volume (L)	33	33	33	33	33	33
concentration in normal train (ppmvd)	1.1	2.1	3.5	12.4	BDL	1.1
concentration in spiked train (ppmvd)	2.1	2.4	6.1	13.2	0.7	9
normal train (ug)	77.0	115.4	131.3	495.8	BDL	129.2
spiked train (ug)	161.6	145.1	251.6	580.6	55.8	1162.7
field spike (ug)	70	800	118	487	41	1200
Equivalent Spiking Level (ESL) (ppmvd)	0.91	13.23	2.86	11.07	0.51	9.29
ESL, % of actual source gas concentration	83%	630%	82%	89%	not calculated, normal train BDL	844%
Does ESL meet criteria?	yes	no	yes	yes	not calculated, normal train BDL	no
percent difference	17%	not calculated, ESL criteria not met	18%	11%	not calculated, normal train BDL	not calculated, ESL criteria not met
low spike recovery (%)	110%	not calculated, ESL criteria not met	91%	7%	not calculated, normal train BDL	not calculated, ESL criteria not met
High Level Run Spike (High Level Spiked Sample Train)						
normal sample train sample volume (L)	29	29	29	29	29	29
spiked sample train sample volume (L)	30	30	30	30	30	30
concentration in normal train (ppmvd)	1.3	1.9	4.1	13.2	0.5	BDL
concentration in spiked train (ppmvd)	13.6	15.3	34.3	100	20.4	9
normal train (ug)	87.9	101.0	148.6	510.2	35.0	BDL
spiked train (ug)	951.4	841.1	1286.3	3998.3	1478.6	1057.0
field spike (ug)	1050	800	118	4000	470	1200
Equivalent Spiking Level (ESL) (ppmvd)	15.01	14.55	3.15	100.04	6.48	10.22
ESL, % of actual source gas concentration	1155%	766%	77%	758%	1297%	not calculated, normal train BDL
Does ESL meet criteria?	no	yes	yes	yes	no	not calculated, normal train BDL
percent difference	not calculated, ESL criteria not met	666%	23%	658%	not calculated, ESL criteria not met	not calculated, normal train BDL
high spike recovery (%)	not calculated, ESL criteria not met	92%	960%	87%	not calculated, ESL criteria not met	not calculated, normal train BDL
Bracketed spike recovery	110%	92%	91%	7%	not calculated, low spike BDL, high spike did not meet ESL criteria	not calculated, high spike BDL, low spike did not meet ESL criteria
Alternate Value *			525%	47%		
Successful spike and recovery?	yes	yes	yes	no	no	no

* Section 2.4.2.5.3.2, Rule 3 allows the user to average spike recoveries or to use the spike with the smallest percent difference

WORKSHEET FOR DETERMINING THE SPIKE RECOVERY QA PROCEDURE FOR IM/CAN/WP-99.02

Step 1: Calculate Equivalent Spiking Levels

$$\text{ESL} = \text{mass}_{\text{field spike}} \div \text{MW} \times 24.055 \text{ L/gmol} \div \text{V}_{\text{run spike sample}}$$

	Mass, µg	MW, g/gmol	$V_{\text{run spike sample}}$, dsL
LESL			
HESL			

$$\text{LESL} = \frac{(\qquad \text{ug}) \times 24.055\text{L/gmol}}{(\qquad \text{g/gmol}) \times (\qquad \text{L})} = _______ \text{ppmvd}$$

$$\text{HESL} = \frac{(\qquad \text{ug}) \times 24.055\text{L/gmol}}{(\qquad \text{g/gmol}) \times (\qquad \text{L})} = _______ \text{ppmvd}$$

Step 2. Sample Train Results

Spike Level	ESL, ppmvd	Normal Train (C_A), ppmvd	5 x C_A Ppmvd	10 x C_A ppmvd	Spike Train, (C_{ST})ppmvd
Low Bracket					
High Bracket					

Step 3. Spike Recovery Determination

- If using the bracketed run spike option, then the rules for the determining the spike recovery are:

Rule 1. Use this rule if both criteria are YES: (enter values)

Is LESL	>	$5xC_{A\ Low}$?	Yes/No
	>		

Is HESL	#	$10xC_{A\ High}$?	Yes/No
	#		

$$\text{If Yes, spike recovery} = \frac{[C_{\text{ST High}}(ppmvd) - C_{\text{A High}}(ppmvd)]}{\text{HESL}(ppmvd)} \times 100$$

$$= \frac{(\qquad \text{ppmvd} - \qquad \text{ppmvd})}{_______ \text{ ppmvd}} \times 100 = _________ \%$$

Rule 2. Use this rule if both criteria are <u>YES</u>: (enter values)

Is LESL	#	5x$C_{A\ Low}$?	Yes/No
	#		

Is HESL	>	10x$C_{A\ High}$?	Yes/No
	>		

$$\text{If Yes, spike recovery} = \frac{[C_{ST\ Low}(ppmvd) - C_{A\ Low}(ppmvd)]}{\text{LESL}(ppmvd)} \times 100$$

$$= \frac{(\quad\quad \text{ppmvd} - \quad\quad \text{ppmvd})}{_____\ \text{ppmvd}} \times 100 = _________\%$$

Rule 3. Use this rule if both criteria are <u>YES</u>: (enter values)

Is LESL	#	5x$C_{A\ Low}$?	Yes/No
	#		

Is HESL	#	10x$C_{A\ High}$?	Yes/No
	#		

$$\text{(3a) LESL Spike Recovery} = \frac{[C_{ST\ Low}(ppmvd) - C_{A\ Low}(ppmvd)]}{\text{LESL}(ppmvd)} \times 100$$

$$= \frac{(\quad\quad \text{ppmvd} - \quad\quad \text{ppmvd})}{______\ \text{ppmvd}} \times 100 = ______\%$$

$$\text{(3b) Low Spike \%difference} = \text{ABS}\left|\frac{\text{LESL(ppmvd)} - C_{A\ Low}\text{(ppmvd)}}{C_{A\ Low}\ \text{(ppmvd)}}\right| \times 100$$

$$= \text{ABS}\left|\frac{\quad - \quad}{\quad}\right| \times 100 =$$

$$\text{(3c) ESL}_{High}\ \text{Spike Recovery} = \frac{[C_{ST\ High}(ppmvd) - C_{A\ High}(ppmvd)]}{\text{HESL}(ppmvd)} \times 100$$

$$= \frac{(\quad\quad \text{ppmvd} - \quad\quad \text{ppmvd})}{______\ \text{ppmvd}} \times 100 = _______\%$$

$$\text{(3b) High Spike \%difference} = \text{ABS}\left|\frac{\text{HESL(ppmvd)} - C_{A\ High}\text{(ppmvd)}}{C_{A\ High}\ \text{(ppmvd)}}\right| \times 100$$

$$= \text{ABS}\left|\frac{\quad - \quad}{\quad}\right| \times 100 =$$

Choices for Rule #3 Spike Recovery:

Choice 1: Use average of LESL Spike Recovery (3a) and HESL Spike Recovery (3c)

$$= \frac{\left[(high)\qquad\%+(low)\qquad\%\right]}{2} = _______\%$$

Choice 2: Use the ESL with the smallest *spike %difference* to calculate the spike recovery,

Which ESL Spike %difference is smaller? (circle one)

LESL Spike %difference (Step 3.3b) or HESL Spike %difference (Step 3.3d) ?

Then use (H or L)ESL Spike Recovery result from Step 3.3a or 3c = _______%

Which choice is going to be used? (circle on)

Choice #1 or Choice #2

Selected Spike Recovery from Choice # _____ for Step 3 = _________%

Rule 4.

Is LESL	>	$5xC_{A\ Low}$?	Yes/No
	>		

Is HESL	>	$10xC_{A\ High}$?	Yes/No
	>		

If the answer to both is "YES," then ESLs do not meet the criteria and spike recovery should not be calculated and reported. Report, instead, that the spike equivalent levels did not meet the Bracketed Spike Run Criteria.

SUMMARY OF QUALITY ASSURANCE PROCEDURES

Field Quality Assurance Procedures

Procedure	Method Section	Criteria
Field Blank	7.1	None
Duplicate Sample Run	7.4	Table 7.1
Run Spike	7.5	Table 7.3 and Section 7.5.5
Train Spike	7.6	Section 7.6.3
Equivalent Spiking Level	7.5.3	Table 7.2 and Section 7.5.5
Field Spike	7.3	None
Leak Check	6.5	Section 6.5.1
Sample Flow Check	6.6 and 6.8	Sections 6.6 and 6.8
Equipment Blank	7.2	None

Laboratory Quality Assurance Procedures

Procedure	Method Section	Criteria
Lab Blank	8.2.3.1, 8.3.3.1, 8.4.3.1 and 8.5.3.1	None
Calibration Verification Standard	8.2.3.3, 8.3.3.3, 8.4.3.3, and 8.5.3.3	Sections 8.2.3.3, 8.3.3.3, 8.4.3.3 and 8.5.3.3
Laboratory Duplicates	8.2.3.2, 8.3.3.2, 8.4.3.2, and 8.5.3.2	Sections 8.2.3.2, 8.3.3.2, 8.4.3.2, and 8.5.3.2
Matrix Spike Recovery	8.2.3.5 and 8.4.3.5	Sections 8.2.3.5 and 8.4.3.5
Second Source or Reference Standard	5.16, 8.2.3.4, 8.3.3.4, and 8.4.3.4	Sections 8.2.3.4, 8.3.3.4, and 8.4.3.4
Calibration Check	8.2.2, 8.3.2, 8.4.2, and 8.5.2	Sections 8.2.2, 8.3.2, 8.4.2, and 8.5.2