CALIFORNIA
AIR RESOURCES BOARD

Industrial Strategies Division
Oil and Gas and Greenhouse Gas Mitigation Branch

# Air Sampling and Analysis Plan for Well Stimulation Treatment Operations for xxxxxxxx Wells API #xxxxxxx

July 2018

Prepared by:

Program Assessment Section

This page intentionally left blank.

**Air Sampling and Analysis Plan for**
**Well Stimulation Treatment Operations**

**Reviewed by:**

California Air Resources Board, Industrial Strategies Division

California Air Resources Board, Monitoring and Laboratory Division

California Air Resources Board, Research Division

Department of Conservation, Division of Oil and Gas and Geothermal Resources

William T. Stringfellow, PhD., Lawrence Berkeley National Laboratory

Abbreviations

| | |
|---|---|
| AM | Ambient Air |
| API | American Petroleum Institute |
| ASTM | American Society for Testing and Materials |
| BK | Background |
| CARB | California Air Resources Board |
| CAS | Chemical Abstract Services |
| COC | Chain of Custody |
| Dup | Duplicate (sample) |
| DNPH | Dinitrophenylhydrazine |
| DOGGR | Department of Oil, Gas, and Geothermal Resources |
| EPA | U.S. Environmental Protection Agency |
| GHG | Greenhouse Gas |
| Hg | Mercury |
| ID | Identification |
| L | Liter |
| MFC | Mass Flow Control |
| MS | Matrix Spike |
| MDL | Method Detection Limit |
| NELAP | National Environmental Laboratory Accreditation Program |
| NIOSH | National Institute for Occupational Safety and Health |
| PAH | Polycyclic Aromatic Hydrocarbons |
| psig | Pound Per Square Inch Gauge |
| PST | Pacific Standard Time |
| PUF | Polyurethane Foam |
| RPD | Relative Percent Difference |
| SIM | Selective Ion Monitoring |
| TAC | Toxic Air Contaminant |
| TB | Trip Blank |
| TIC | Tentatively Identified Compounds |
| $ug/m^3$ | Micrograms per Cubic Meter |
| VOC | Volatile Organic Compound |
| WST | Well Stimulation Treatment |
| XAD | Adsorbent Ion Exchange Resin |

## Table of Contents


**1.0 INTRODUCTION ..... 1**
1.1 Background ..... **1**
1.2 Project Goals and Objectives ..... **2**
**2.0 SAMPLING MEDIA AND INSTRUMENTATION ..... 2**
2.1 Meteorological Station ..... **5**
**3.0 SAMPLING LOCATIONS ..... 5**
3.1 WST Operation Sampling Stations ..... **8**
3.2 Background Sampling Stations ..... **10**
**4.0 QUALITY CONTROL ..... 12**
4.1 Sample Identification ..... **13**
4.2 Sample Handling and Transportation ..... **13**
**5.0 LABORATORY ANALYSIS ..... 14**
5.1 Analysis Procedures ..... **14**
**6.0 DELIVERABLES ..... 15**
6.1 Contact Information ..... **15**
6.2 WST Air Sampling and Analysis Report ..... **17**


**Tables** **Page**


TABLE 1: Suggested Sample Media and Sample Duration…….....11
TABLE 2: Quantity of Sampling Media Needed per Sampling Event….....12


**Figures** **Page**


Figure 1: Example of a Passive Canister Sampler…….....4
Figure 2: Example of Active Sorbent Tube Sampler ..…… …….....4
Figure 3: Example of a Site Plan View Map with Suggested Air Sample Station Locations…..…….....…….....…….....6
Figure 4: Example Data Sheet for Collecting Air Samples in Canisters…….....16


**Attachments**


**Attachment A** Volatile Organic Compounds Required to be Included in Analysis (Suggested EPA Method Modified TO-15)

**Attachment B** Aldehydes Required to be Included in Analysis (Suggested EPA Method Modified TO-11A)

**Attachment C** PAHs/Semi-Volatile Organic Compounds Required to be Included in Analysis (Modified EPA Method TO-13A SIM or similar method as approved by CARB)

**Attachment D** Other Compounds Required to be Included in Analysis (Suggested Method ASTM D-1945/3588, Suggested Method NIOSH 5523)

## 1.0 INTRODUCTION

Well stimulation treatment (WST) operations in oil and gas fields emit volatile organic compounds (VOCs), toxic air contaminants (TACs), greenhouse gases (GHGs), and other criteria pollutants. Limited information is available for the identification and quantification of emissions and fugitive vapors during WST operations in California. The primary goal of this Air Sampling and Analysis Plan for Well Stimulation Treatment Operations (Air Sampling Plan) is to specify methods and procedures to be used to create a site-specific air sampling plan (Site-Specific Air Sampling Plan) that will be used to collect specific compounds for laboratory analysis. Suggested sampling media and analytical methods are included in this document.

This Air Sampling Plan is designed to be used to prepare the Site-Specific Air Sampling Plan used to identify air contaminants present before and during WST events. Potential air contaminants include compounds injected into the well as components of well stimulation fluid, compounds commonly found in oil and gas operations and released into the atmosphere during production, compounds released during the operation of equipment associated with the WST operation, and products of chemical reactions that occur underground because of a WST event. Air contaminants from well stimulation activities may be released to the atmosphere during well circulation events, fluid spills, or through fugitive leaks, among other pathways.

This Sampling Plan outlines specific procedures to collect air samples before and during a WST operation and to analyze the samples for VOCs, TACs, GHG emissions, and other compounds of interest. The air sampling methodologies described in this document are based on air sampling protocols and information provided in such documentations as the Environmental Protection Agency's (EPA) Methods 325A and 325B for Passive Fenceline Monitoring for Fugitive and Area Sources[1], Air Quality and Land Use Handbook: A Community Health Perspective[2], and 40 CFR 58[3].

### 1.1 Background

Well stimulation is performed on an oil or gas well to enhance reservoir flow paths and increase production by improving the flow of hydrocarbons. Well stimulation occurs after the well has been drilled and the drill rig has been removed, but generally before the well goes into production. This Air Sampling Plan will be used to help prepare the Site-Specific Air Sampling Plan for use before and during one of three types of well stimulation treatments: hydraulic fracturing, acid fracturing, and acid matrix stimulation.

Hydraulic fracturing involves the injection of fluids, chemicals, and other materials into a well at pressures capable of fracturing rocks in the oil or gas reservoir formation.

1 http://www3.epa.gov/airtoxics/petrefine/RefineryRTR2060-AQ75Final_9-28-15disclaimer.pdf.
2 California Environmental Protection Agency, California Air Resources Board, 2005.
3 40 CFR Part 58 - Ambient Air Quality Surveillance. https://www.law.cornell.edu/cfr/text/40/part-58.

During the WST event, fractures or voids in the rock formation are filled with sand (proppant) to keep them open, improving productivity of the oil and/or gas well. Acidic fluids, used in acid fracturing or acid matrix stimulation, are pumped or injected into the reservoir formation to open up or dissolve channels in the formation, allowing the oil and/or gas trapped in the formation to flow more freely to the wellbore. Some materials used in the WST operation include water, acid, chemicals, special polymer gels, and sand.

The sampling site (Site) as defined in this Air Sampling Plan includes the wellhead, equipment staging area, and any wastewater storage vessels such as circulation tanks or storage containers affiliated with the WST event. The equipment staging area includes the well stimulation pumping equipment, proppant containers (e.g. sand), containers with various fluids and chemicals, and other equipment. Generally the equipment staging area and wellhead are located in the same area however, they may be located several thousand feet apart.

A WST event can last for several days depending on the number of zones that are proposed to be stimulated in the well. The WST event can be delayed, in some cases for days, and therefore the schedule for air sampling at the Site must be flexible. The detailed Site-Specific Air Sampling Plan is intended to be used to collect air samples during one day (8 to 24 contiguous hours) of the WST event, even if the WST operation will occur over several days.

### 1.2 Project Goals and Objectives

The goals of this Air Sampling Plan are to provide recommended test methods and procedures necessary to collect air samples in oil and gas fields before and during WST events, transport air samples to a laboratory for analysis, and analyze the sample media for chemical composition. To achieve the project goals, the following objectives must be met:

1. Appropriate application of air sampling equipment and laboratory analysis to determine background ambient chemical concentrations at a specified location in the vicinity of the Site prior to a WST operation and at another location outside the influence of the WST operation.
2. Appropriate application of air sampling equipment and laboratory analysis to determine chemical concentrations of selected constituents in the air surrounding the Site during a WST operation.
3. Application of relevant quality assurance/quality control practices during sample collection and in the laboratory to ensure the integrity of the air samples.

## 2.0 SAMPLING MEDIA AND INSTRUMENTATION

**Sampling media must be capable of capturing all compounds listed in Attachments A through D**. To provide media capable of collecting the wide variety of compounds potentially present during a WST event, several sampling media types must be used. The following sampling media are examples of what should be used to

collect air samples during the WST sampling event. The laboratory will dictate which sampling media is appropriate, based on the compounds that are required to be analyzed for each WST event (see Attachments A through D) and how the sampling equipment should be used.

- Vacuum Canisters (e.g. Summa)
- Sorbent tube with multiple sorbent materials
- DNPH cartridge (2,4-dinitrophenylhydrazine)
- PUF/XAD cartridge* (polyurethane foam/adsorbent ion exchange resin)
- XAD-7 tube
- Silica gel tube
- Tedlar Bag
- Charcoal tube

*Or similar media as approved by CARB

Each media type captures and detects a broad range of air pollutants. The media selected for the sampling plan were chosen based on the need for relatively low compound detection limits and short duration of the sampling period (8 to 24 contiguous hours). Detection limits for laboratory analysis are required to be **less than one microgram per cubic meter (ug/m$^3$)** for most analysis to assess any potential health hazards.

To achieve the detection limit, sorbent tubes and cartridges may require active pumped sampling. Selection of pump type and calibration for the active samples will be determined by the laboratory and will depend on the sampling media, pumping rate, and the duration of the sample collection (approximately 8 to 24 contiguous hours).

Active samples are collected using a pump to pull air into the canister or tedlar bag or across the sorbent media at a constant flow rate. While active canister samples can provide more volume of sampled air and greater stability for some compounds, they can also contaminate the sample if the pump and instrument inlet system are not clean (an example of a passive canister sampler is shown in Figure 1).

The sorbent tubes and cartridges may require a pump in order to pass a sufficient volume of air over the media for the short sample duration period (an example of a pumped sorbent tube is shown in Figure 2). In general, the active sorbent tube and cartridge samples will be collected by pumping air at a constant flow rate through a bed of sorbent(s) or other media (e.g. PUF/XAD or DNPH) for approximately 8 to 24 contiguous hours. The analytical laboratory should be consulted about proper flow rates for the pumps based on the sorbent media and final reporting limit for the compounds and methods (ug/m$^3$). The proper sampling rate must be used to prevent breakthrough of the chemical through the sorbent material.

The intake to the sampling media (canisters or sorbent tubes and cartridges) must be elevated approximately 5 to 6 feet (1.5 to 1.8 meters) above the ground surface during the sample event (Figures 1 and 2).

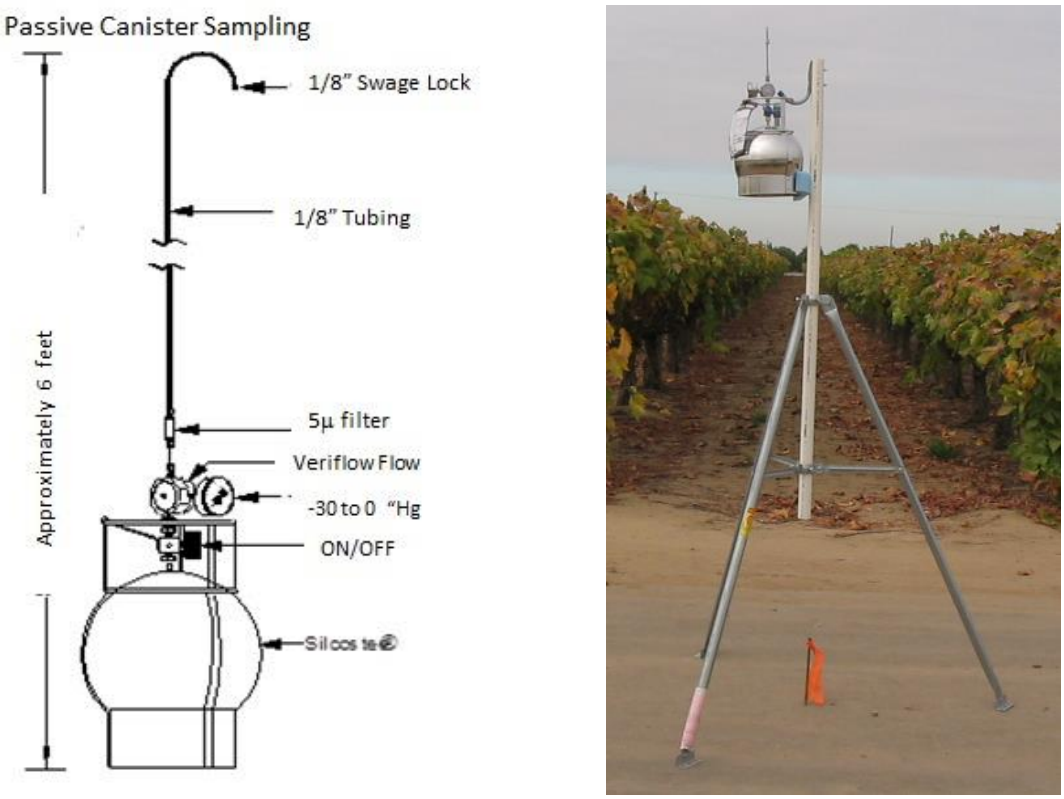



**Figure 1:** Example of a passive canister sampler.

**Figure 2:** Example of an active sorbent tube sampler.

## 2.1 Meteorological Station

The meteorological station collects and documents weather data during the background air sampling event and during the WST air sampling event. The meteorological station can be a portable or temporary meteorological station or a nearby (within five miles) permanent meteorological station. The meteorological station will be equipped with the basic suite of sensors to measure the following:

- wind direction and velocity
- barometric pressure
- temperature
- relative humidity
- precipitation

The daytime prevailing wind direction must be determined from nearby weather stations or from the temporary meteorological station prior to setting up the air sampling stations. The background sample station will be located upwind of the WST Site. The primary sampling station downwind of the Site will consist of a primary sample station, a matrix spike (MS) sample station and a duplicate (Dup) sample station.

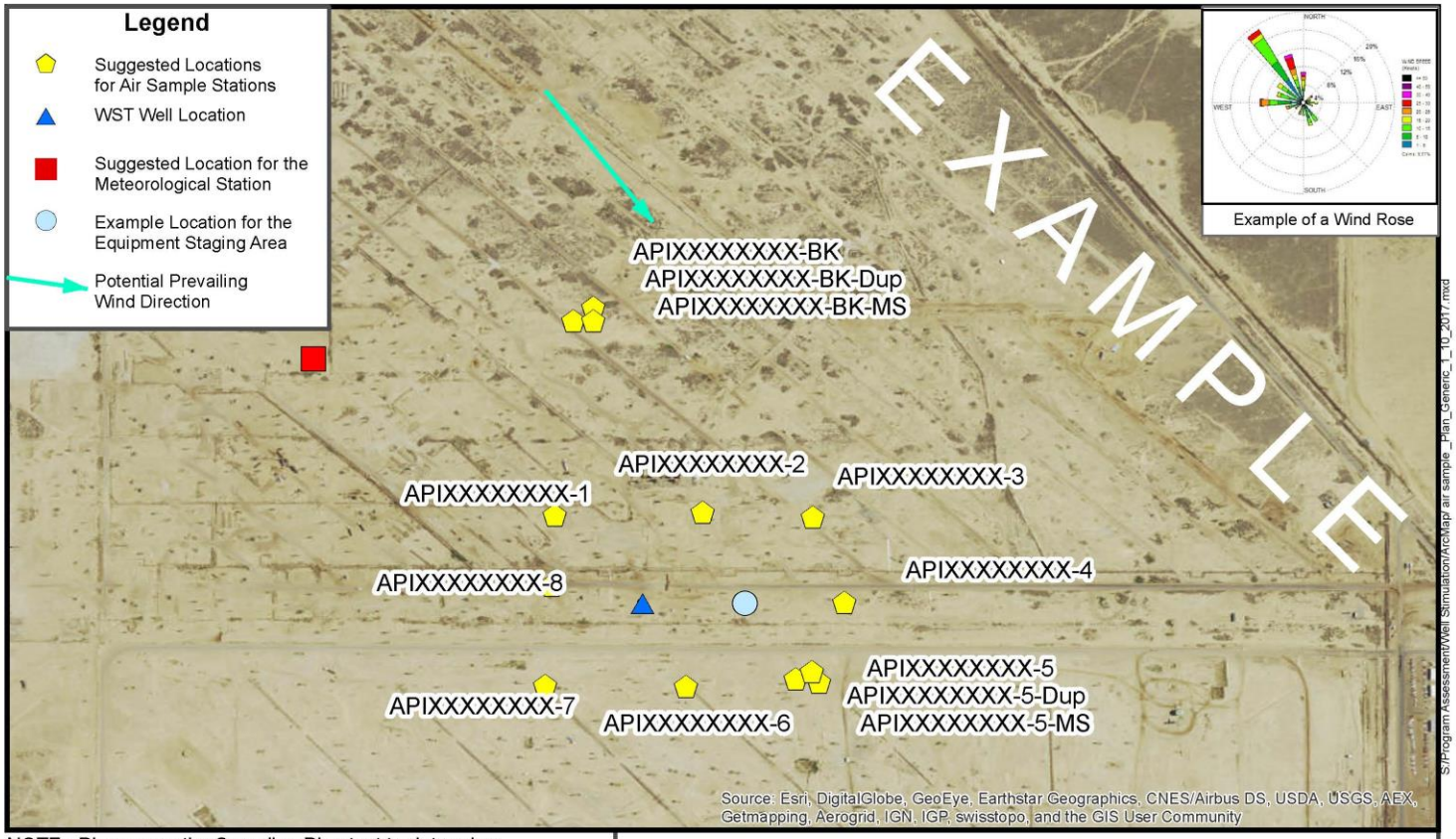
The meteorological station(s) should be set up to collect and record data during all phases of air sampling, background air sampling, and during the WST air sampling events. Useful guidance is provided in EPA-454/B-08-002, Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV: Meteorological Measurements, Version 2.0 (Final), March 2008[4].

## 3.0 SAMPLING LOCATIONS

The intent of the Site-Specific Air Sampling Plan is to collect background air samples as non-source affected measurements not associated with a WST event and air samples taken during and associated with a WST event. The Site for the WST event is defined as the wellhead, circulation tanks, and equipment staging. An example of the Site area is presented in Figure 3. The equipment staging area may, in some cases, be located several thousand feet from the wellhead. A minimum of eight air sampling station locations are required to be set up on in a perimeter around the Site (Figure 3). If possible, when the terrain is hilly, the sampling stations should be set up at a similar elevation as the average elevation of the WST Site. If this is not possible, then the sample stations should be set up at approximately 300 feet from the Site.

An aerial photograph or Site map should be used to prepare a Site plan map, similar to the example presented in Figure 3. The Site plan map must present the locations

4 http://www3.epa.gov/ttn/amtic/met.html




NOTE: Please see the Sampling Plan text to determine the locations of the oilfield background (BK) sample station and the ambient air (AM) background sample station.

Scale
0 500 1,000
Feet

N

**Figure 3. Example of Site Plan View Map with Suggested Air Sample Station Locations**

**Well API #XXXXXXXX**

This page intentionally left blank.

of the air sample stations and must be included in the WST Air Sampling and Analysis Report provided to the CARB.

Prior to setting up the sampling stations, any obstacles or obstructions (buildings, roads, and fences), hills, and other terrain issues (e.g., bodies of water or swamp land) that could interfere with air flow to the sampler or that prevent reasonable access to a sample location should be identified during a Site visit. General guidance for air sampling locations can be found in EPA-454/B-13-003, Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Ambient Air Quality Monitoring Program, May 2013[5]. Complex topography and physical site obstructions that may prevent access to a planned air sampling location should be documented and reported in the WST Air Sampling and Analysis Report. Potential off-Site source interferences (e.g., neighboring industrial facilities, transportation facilities, fueling operations, combustion sources, short-term transient sources, residential sources, nearby highways) should also be reported in the WST Air Sampling and Analysis Report.

The following items should be addressed and included in the WST Air Sampling and Analysis Report:

- Conduct a site visit or consult a plan view map of the Site to determine size and shape of the footprint of the Site and the location of perimeter sampling locations.
- Identify obstacles or obstructions that could impede air flow at the Site, modify the sampling stations accordingly, and document in the WST Air Sampling and Analysis Report.
- Identify, if possible, nearby or upwind sources of target emissions and document.
- Identify the upwind location for the background sample and the downwind location for a duplicate sample.

### 3.1 WST Operation Sampling Stations

It is suggested that each sampling station consist of one DNPH cartridge, one 6 liter canister, one XAD-7 tube, and one PUF/XAD tube (or similar media as approved by CARB). Other sampling media may be used to collect samples for specific analytes, such as a tedlar bag for the carbonyl sulfide, as long as the sampling and analysis procedures are suitable to detect at a minimum the compounds specified in Attachments A through D at detection limits of less than 1 $\mu g/m^3$. More sampling canisters or sorbent tubes may be required at each sampling station based on the laboratory's specifications. Cartridges, sorbent tubes, and canisters may require special housing for protection from ambient conditions depending on the laboratory and/or manufacturer's specifications. Laboratory and manufacturer's specifications for the sampling equipment, pumps and housings will be used as a guide for proper use of the sampling apparatus.

5 http://www3.epa.gov/ttnamti1/files/ambient/pm25/qa/QA-Handbook-Vol-II.pdf

A minimum of eight sample stations will be used to collect air around the perimeter of the Site during the WST event (perimeter samples). The perimeter samples will be collected about 300 feet from the well head and circulation tank and/or the equipment staging area at Sites with relatively flat terrain. Sampling station locations will vary based on the topography at Sites with hilly terrain. The Site includes the equipment staging area, the wellhead, and the circulation tanks (Figure 3). The duplicate sample (Dup) and the matrix spike (MS) samples will be placed at the sampling location with the expected maximum concentration of air contaminants coming from the Site, typically downwind of the WST activities as shown on Figure 3.

Air sample collection will begin when chemicals are being mixed prior to injection into the stimulated zone and continue during well circulation or well cleanout and flow back activities, if practical. If well circulation and cleanout are performed after the last stage of WST, then that stage will be targeted for air sampling so the air samples can be collected during chemical mixing, well stimulation, well cleanout, and circulation events.

Each Site will be different and the Site-Specific Air Sampling Plan will discuss the rationale for the duration of time needed to collect air samples in order to have detection limits of less than 1 ug/$m^3$. Air sampling should coincide with as many well stimulation and cleanout activities as possible in a 24-hour period, including:

- Chemical Mixing
- Well stimulation
- Circulation or well clean out
- Flow back, if applicable.

Air sample collection will continue for 8 to 24 hours continuously after air sampling has begun. The duration of time for the air sampling event will depend on the amount of time it takes for chemical mixing, well stimulation, and subsequent well cleanout.

In summary, each WST air sampling event should include, at a minimum, the suggested set of sample equipment:

- 8 perimeter sample stations (8 canisters, 8 DNPH tubes, 8 PUF/XAD tubes*, 8 XAD-7 tubes)
- 1 duplicate sample station (1 canister, 1 DNPH tube, 1 PUF/XAD tube*, 1 XAD-7 tube)
- 1 matrix spike sample station (1 DNPH tube, 1 PUF/XAD tube*, 1 XAD-7 tube)
- 1 trip blank sample (1 canister, 1 DNPH tube, 1 PUF/XAD tube*, 1 XAD-7 tube: not deployed in the field)
- 1 trip spike sample (1 DNPH tube, PUF/XAD tube*, 1 XAD-7 tube: all media spiked, not deployed in the field)

*Or similar media as approved by CARB

The list above does not include the background sample stations discussed below and included in Tables 1 and 2. The duplicate (side-by-side) air sample station will be located alongside the predominantly downwind perimeter sample station (Figure 3).

More than one type of sample media (e.g. several canisters) may be required by the laboratory to collect air samples over the time period.

The matrix spike will be prepared in the laboratory by injecting a known concentration of a target compound(s) into each type of cleaned and undamaged sampling media. The matrix spike will be sampled in parallel with the primary air samples and located at the duplicate air sample station at the predominantly downwind air sample station. The matrix spike sample media will be handled and analyzed identically to the primary sample media.

One set of trip blanks and one set of trip spikes will accompany the samples for each WST event (see Tables 1 and 2). A trip spike will be prepared by the laboratory by injecting a known concentration of a target compound(s) into cleaned and undamaged sampling media. A trip blank will be a cleaned and undamaged sampling media. The trip spike and trip blank will not be deployed in the field; they will accompany the sample media shipment to the field and back to the laboratory unopened.

### 3.2 Background Sampling Stations

The background air samples are intended to analyze the quality of the non-source affected media, air not associated with the designated (or any other) WST event. Two background sample stations will be used to collect air samples outside of the influence of the well undergoing WST.

- The oilfield air background (BK) sample station must be located in the vicinity of the WST event, at least 500 feet upwind or crosswind from the WST.
- The ambient air background (AM) sample station must be located outside of the influence of any oil and gas field. This sampling station may be located up to 8 miles away to avoid the influence of oil and gas production and other potential emission sources, and at least 500 feet from a major roadway.

The sampling duration for the background air samples should be similar to the sampling duration for the WST air samples, approximately 8 to 24 contiguous hours. The background air samples will be collected at least 24 hours prior to the WST event. The background sample stations will be placed in a safe location where they will not be vandalized or damaged. Details of and rationale for the placement of the background sampling stations should be noted in the WST Air Sampling and Analysis Report.

The oilfield air background sample station (BK) will include the following set of sampling equipment:

- 1 sample station (1 canister, 1 DNPH tube, 1 PUF/XAD tube*, 1 XAD-7 tube)
- 1 duplicate sample station (1 canister, 1 DNPH tube, 1 PUF/XAD tube*, 1 XAD-7 tube)
- 1 matrix spike sample station (1 DNPH tube, 1 PUF/XAD tube*, 1 XAD-7 tube)

*Or similar media as approved by CARB

The ambient air background sample station (AM) will include the following set of sampling equipment:

- 1 sample station (1 canister, 1 DNPH tube, 1 PUF/XAD tube*, 1 XAD-7 tube)
- 1 duplicate sample station (1 canister, 1 DNPH tube, 1 PUF/XAD tube*, 1 XAD-7 tube)
- 1 matrix spike sample station (1 DNPH tube, 1 PUF/XAD tube*, 1 XAD-7 tube)

*Or similar media as approved by CARB

One trip blank and one trip spike is all that is necessary for the air sampling event, unless the laboratory advises otherwise.

**Table 1: Suggested Sample Media and Sample Duration**

| Sample Type | Sample Media / Sample Duration Time |
|---|---|
| **Background Samples** | |
| **Oilfield Air Background Sample (BK)** | 1 canister (6L), 1 DNPH tube, 1 PUF/XAD tube*, 1 XAD-7 tube / ~8-24 hours |
| Matrix Spike Sample | Spiked : 1 DNPH tube, 1 PUF/XAD tube*, 1 XAD-7 tube / ~8-24 hours |
| Duplicate Background Sample | 1 canister (6L), 1 DNPH tube, 1 PUF/XAD tube*, 1 XAD-7 tube / ~8-24 hours |
| **Ambient Air Background Sample (AM)** | 1 canister (6L), 1 DNPH tube, 1 PUF/XAD tube*, 1 XAD-7 tube / ~8-24 hours |
| Matrix Spike Sample | Spiked : 1 DNPH tube, 1 PUF/XAD tube*, 1 XAD-7 tube / ~8-24 hours |
| Duplicate Background Sample | 1 canister (6L), 1 DNPH tube, 1 PUF/XAD tube*, 1 XAD-7 tube / ~8-24 hours |
| **WST Sampling Event** | |
| Perimeter Samples | 8 canisters (6L), 8 DNPH tubes, 8 PUF/XAD tubes*, 8 XAD-7 tubes / ~8-24 hours |
| Duplicate Sample | 1 canister (6L), 1 DNPH tube, 1 PUF/XAD tube*, 1 XAD-7 tube / ~8-24 hours |
| Matrix Spike Sample | Spiked : 1 DNPH tube, 1 PUF/XAD tube*, 1 XAD-7 tube / ~8-24 hours |
| Trip Spike Sample | Spiked : 1 DNPH tube, 1 PUF/XAD tube*, 1 XAD-7 tube / ~8-24 hours / not deployed in the field |
| Trip Blank | 1 canister (6L), 1 DNPH tube, 1 PUF/XAD tube*, 1 XAD-7 tube / ~8-24 hours /not deployed in the field |

*Or similar media as approved by CARB

**Table 2: Quantity of Sampling Media Needed per Sampling Event**

| Sample Media | Total Number of Media | Suggested Analysis |
|---|---|---|
| **6L canisters** | **15 canisters** (total) – 8 perimeter, 2 background, 3 duplicate, 1 trip blank, 1 extra (not analyzed unless deployed) | Analysis EPA Modified TO-15, ASTM D1945/3588 (see Attachments A and D) |
| **DNPH Tubes** | **19 sorbent tubes** (total) – 8 perimeter, 2 background, 3 duplicate, 3 matrix spikes, 1 trip blank, 1 trip spike, 1 extra (not analyzed unless deployed) | Analysis TO-11A Compendium for all Aldehydes (see Attachment B) |
| **PUF/XAD tube*** | **19 tubes** (total) – 8 perimeter, 2 background and 3 duplicate, 3 matrix spikes, 1 trip blank, 1 trip spike, 1 extra (not analyzed unless deployed) | Analysis TO-13A or similar method as approved by CARB (see Attachment C) |
| **XAD-7 tube** | **19 tubes** (total) – 8 perimeter, 2 background and 3 duplicate, 3 matrix spikes, 1 trip blank, 1 trip spike, 1 extra (not analyzed unless deployed) | NIOSH Method 5523 for Ethylene Glycol (see Attachment D**)** |

***Or similar media as approved by CARB**

## 4.0 QUALITY CONTROL

The air samples will be collected by competent and experienced personnel that have experience collecting air samples in a similar environment and can identify existing and potential hazards in the field. The samples must be collected using methodology that is scientifically sound and sampling and analytical methods that are sufficiently accurate and precise and can be repeated in order to corroborate the sampling procedures and results at a future time.

Quality control procedures must be observed to ensure the integrity of air samples collected in the field. All samples will be analyzed by a laboratory certified under the National Environmental Laboratory Accreditation Program (NELAP). Sample custody is an important aspect of any sampling program, and sample custody procedures must be strictly followed to assure that unadulterated, representative, and secure samples and sample media are delivered both to and from the sampling location. Chain of Custody (COC) sheets, provided by the laboratory, will be utilized to track the samples in the field.

Duplicate samples are collected by placing a set of air sampling media in the same location as the normal or primary sampling media, as defined and specified in 40 CFR 58. If the primary sampling media does not operate correctly, or the collected data is invalid, valid duplicate data can be substituted for the samples missed by the primary sampling media. If acceptance criteria are exceeded for the primary air samples or the duplicate air samples, then sample and analysis techniques are investigated to determine the cause(s) of the exceedance.

## 4.1 Sample Identification

Each sample media will be assigned a field sample number that identifies the Site (API Number), the sample ID number, and sample information. The nomenclature for the sampling locations will start at the northwest corner of the perimeter line and proceed in numerical order clockwise around the perimeter. The perimeter line will surround the wellhead, circulation tanks, and equipment staging area. The sample name will include all or part of the well API number and a location number. For example, as shown on Figure 3, the sample collected on the northwest corner of the perimeter line for a site with an API number of API# will be named API#-1, and the next sample location clockwise will be named API#-2. If more than eight sample locations are used around the perimeter of the Site, the samples will be numbered sequentially in the clockwise order and the locations will be presented on the Site plan view map that will be included in the WST Air Sampling and Analysis Report. The following is a generic naming of the sampling locations:

**Site Naming Examples:**
First sample collected in the northwest corner of the perimeter will be named (API#-1). Samples will be numbered sequentially in a clockwise order from this sample, as stated above. The trip blank that accompanies these samples will be named (API#-TB). The duplicate sample will be named the same as the primary sample collected at this location, except it will have a “Dup” at the end the sample name (API#--X-Dup). The matrix spike will have “MS” at the end of the sample name (API#-X-MS). The oilfield background sample will have “BK” at the end of the sample name (API#-BK) and in the case of the duplicate and field spike background samples (API#-BK-Dup and API#-BK-MS, respectively). The background ambient air sample will have “AM” at the end of the sample name (API#-AM).

## 4.2. Sample Handling and Transportation

Personnel will transport cleaned and undamaged sampling media from the laboratory to the sampling location. Following sample collection, the sampling media will be returned to the laboratory. These samples will not be exposed to extreme conditions or subjected to rough handling that might affect sample integrity.

Prior to removing each sampled media from the sample station for transportation, the sample personnel will ensure that the equipment worked properly and the corresponding sample’s paperwork is completed (e.g. COC). The air samples will be stored in a protected location, and on ice, if required by the analytical method, until they can be transported back the laboratory. The contractor or personnel transporting the sampled media must adhere to the transport/shipping temperature recommended by the laboratory. When received by the laboratory, the samples will be analyzed as soon as possible. All reported sampling times, including meteorological data, will be reported in Pacific Standard Time (PST). Figure 4 is an example of the paperwork used when collecting a canister sample.

## 5.0 LABORATORY ANALYSIS

The actual methods used to collect the air samples depend on the laboratory's chemical classes and analytical methods. The suggested sample collection protocol for the air sample methods are provided in Section 2 (Sampling Media and Instrumentation). At a minimum, the air samples are required to be analyzed for the analytes listed in Attachments A, B, C, and D using the following suggested analytical methods:

1. Full suite of VOCs as identified in EPA Method TO-15 (see Attachment A).
2. Aldehydes as identified in EPA Method TO-11A (see Attachment B).
3. Polycyclic aromatic hydrocarbon (PAH) compounds as identified in EPA Method TO-13A or similar method as approved by CARB (see Attachment C).
4. Methane and other compounds using method ASTM D1945/3588 (see Attachment D). Note the required detection limit is uncommon for this method. This will need to be addressed with the laboratory to ensure the appropriate detection limits are reported.
5. Ethylene glycol using method NIOSH 5523 (see Attachment D).

Note: Some compounds, such as methanol, may be analyzed as tentatively identified compounds (TICs) using method TO-15 SIM, depending on the laboratory.

### 5.1 Analysis Procedures

The quality control and quality assurance objectives are to develop and implement procedures for field sampling, laboratory analysis, and reporting to obtain scientifically valid results. The laboratory will provide cleaned and undamaged sampling media in addition to preparing the necessary trip blanks, trip spikes, and matrix spikes. The laboratory will perform the necessary analyses to measure the concentrations of contaminants in the sampled media and report the findings. Laboratory analyses will be performed in accordance with applicable standard operating procedures.

At least one duplicate sample will be collected simultaneously with a perimeter sample to provide a measure of the reproducibility of the sampling procedures. The results from duplicate analyses are used to evaluate analytical or measurement precision but not the precision of the sampling method or the preservation or storage of the samples.

There must be at least one set of trip blanks for each WST sampling event. Trip blanks consist of canisters, sorbent tubes (XAD-7, PUF/XAD etc.), DNPH cartridges, and/or any other relevant media types. Trip blank results are used as indicators of sample contamination during shipment and storage. Trip blanks are prepared by the laboratory and travel with the shipments to the field and back to the laboratory. The trip blanks are not opened until they are analyzed. The trip blanks are analyzed for the same suite of compounds as the primary samples.

Trip spikes are prepared by the laboratory by injecting a known concentration of a target compound(s) into a cleaned and undamaged sampling media at the same

concentration as the matrix spike. The trip spike is transported and analyzed along with the matrix spike. The trip spike is treated the same as a matrix spike, except that it is not deployed in the field.

Matrix spikes are used to determine if a sample has lost integrity during the transportation of the sample media and during the sampling event. The analytical results from the matrix spike are used to evaluate the integrity of the results from the primary sample. Matrix spikes are prepared by the laboratory by injecting a known concentration of target compound(s) into a cleaned and undamaged sampling media. The matrix spikes are sampled in parallel with the primary samples. The matrix spike sample media is handled identically to the primary sample media deployed in the field.

The following validation and analytical quality control criteria should be followed as dictated by the laboratory.

1. **Sample Hold Time**: Sample hold time criteria will be established by the laboratory. Samples not analyzed within the established hold time will be invalidated by the laboratory.

2. **Duplicate Analysis**: The laboratory will establish relative percent difference (RPD) criteria for duplicate sample analysis. The laboratory will provide the results from the duplicate analyses and RPD.

3. **Method Detection Limit (MDL)**: Analytical results of compounds that are less than the MDL shall be reported as a less than numerical value (<). This less than numerical value shall incorporate any dilutions/concentrations.

4. **Analytical Linear Range**: Any analytical result greater than the highest calibration standard shall be reanalyzed within the calibrated linear range.

## 6.0 DELIVERABLES

A WST Air Sampling and Analysis Report shall document all of the air sampling and analysis for each well stimulation sampling event. The WST Air Sampling and Analysis Report will be delivered within 30 days of the receipt of the analytical data to CARB staff at the following address:

California Air Resources Board
Attention: Carolyn Lozo
1001 I Street
Sacramento CA 95814

## 6.1 Contact Information

For further information or questions please contact:

Luis A. Leyva
Air Pollution Specialist
Luis.leyva@arb.ca.gov

(916) 323-1079

**DRAFT/Working Copy**

## Example Canister Data/Sample Tracking Sheet

Project Name: _____

Site/Sample Name: _____

Operator & Agency: _____

| | | | CANISTER | | LABORATORY | SAMPLER | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Date | Time (PST) | Vacuum ("Hg) | | Pressure or Vacuum | MFC Reading | | Vacuum | |
| | | | LAB | FIELD | | | | | |
| Set-Up | | | | | | | | | |
| Start | | | | | | | | | |
| Stop | | | | | LAB** | | | | |
| | | | | | | | | | |

Type of Sample: [ ] Regular [ ] Duplicate [ ] Spike [ ] Blank [ ] Other

Field Log Number: _____ Canister ID Number: _____ Sampler ID Number: _____

*Observed Unusual Sampling Condition:* [ ] Wind-Blown Sand/Dust [ ] Rain /Fog/Elevated Humidity [ ] Farming Nearby [ ] Construction Nearby [ ] Fire Nearby [ ] Other _____

Field Comments: _____

** = Calibrated Guage Pressure or Vacuum

**Figure 4**: Example data sheet for collecting air samples in canisters.

## 6.2 WST Air Sampling and Analysis Report

The WST Air Sampling and Analysis Report should include, at a minimum, a written report documenting the WST sampling event and a map or Site figure of the air sampling locations.

The report must include:

- Dates and times that the ambient air background (AM) samples were collected and their location.
- Dates and times that the oilfield air background (BK) samples were collected and their location.
- Dates and times that the perimeter air samples were collected and their location.
- Brief description of the well that was stimulated, including operator that owns the well lease, subcontractor performing the WST on the well, API number of the well, well name, latitude/longitude (in coordinate system compatible with the DOGGR system, GCS_North_American_1983), and Public Land Survey System coordinates (township/range/section).
- A log of events happening at the Site, including the time and duration of all WST events, time and approximate duration of any water circulation events to clear proppant from the well, and any other relevant events at the Site or off-Site that could influence the air samples.
- The field sample logs created by the field sampling crew (e.g., names of the sampling team, documentation of the calibration of equipment, times that the sample stations were set up, and duration of sampling).
- The types of sampling media used and specific analytes they targeted.
- All air sampling analytical laboratory results with calculations in hard copy and electronic format.
- A list of the proposed WST chemicals used and the actual WST chemicals used that were injected into the well and their concentration in percent by mass. The operator can provide this information within 30 to 60 days of the WST event.
- The amount of water used for the WST and its source.
- A description of the storage and disposal methods of all water used to clean the proppant from the well after the WST event and/or any fluids pumped from the well and stored at the Site.
- Documentation of any changes to the proposed air sampling station locations. This may include complex topography and physical site obstructions that may have prevented reasonable access to a planned sampling location.
- Any equipment malfunctions.
- Any changes to the final Air Sampling and Analysis plan that was submitted to the CARB for review.
- All meteorological data, especially wind speeds and directions during the sampling event (in tabular form or as a wind rose), and temperature, barometric pressure, relative humidity, and precipitation.
- Any unusual weather patterns such as storms.

- Potential off-Site air contaminant source interferences (e.g., neighboring industrial facilities, transportation facilities, fueling operations, combustion sources, short-term transient sources, residential sources, or nearby highways).
- Pictures showing the setup of an air sampling station used for air sampling at that location.

The sample summary tables should be included in the Report and include all of the analytical results, especially for the compounds listed in Attachments A, B, C, and D and any other detected compounds, the detection limit for all compounds not detected, the date the samples were collected, the analytical method, and the type of sample (e.g. primary, duplicate, trip blank etc.).

The field sample log or field notebook should, at a minimum, contain the following information:

- The time that each sample station was set up.
- The time that air sampling started and was completed at each station.
- The time that chemical mixing started and ended.
- The times when well stimulation started and ended for each zone in the well that was stimulated.
- The times that recirculation started and ended and a description of the circulation mixing tanks and water disposal or reuse method.
- The prevailing wind direction for each of the time frames listed above.
- Any deviations from the work plan that affected the sample collection.
- The names of the personnel performing the sampling.

The laboratory should provide an electronic deliverable along with analytical results of the air sampling.

The Site map included in the WST Air Sampling and Analysis Report should include the following:

- A plan view map of the Site and the approximate location of the perimeter line (the perimeter line should be approximately 300 feet from the wellhead and/or the equipment staging area. See Figure 3).
- The locations of all of the perimeter air sample station locations and their labels or names, including the primary, duplicate, and matrix spike samples.
- The location of the background (BK) air sample.
- The location of the meteorological station.
- Any known obstacles or obstructions that could have impeded air flow at the Site.
- Potential off-Site source interferences (e.g., neighboring industrial facilities, transportation facilities, fueling operations, combustion sources, short-term transient sources, residential sources, or nearby highways, if they are within the scale of the map).

- A wind rose showing the dominant prevailing wind direction during the WST sampling event or a wind chart showing wind direction and speed.
- The location of the well head.
- The locations of water storage and circulation tanks.
- The location of the equipment staging area.
- The API number of the well that was stimulated.
- A scale in feet.
- A north arrow.
- A legend.
- The dates that the air samples were collected.

# ATTACHMENTS

**Attachment A**
**Volatile Organic Compounds Required to be Included in Analysis**
**(Suggested EPA Method Modified TO-15)**

| Analyte | CAS Number |
|---|---|
| Acetone | 67-64-1 |
| Benzene | 71-43-2 |
| Benzyl chloride | 100-44-7 |
| Bromodichloromethane | 75-27-4 |
| Bromoform | 75-25-2 |
| Bromomethane | 74-83-9 |
| 1,3-Butadiene | 106-99-0 |
| Butane | 106-97-8 |
| 2-Butanone (MEK) | 78-93-3 |
| Carbon disulfide | 75-15-0 |
| Carbon tetrachloride | 56-23-5 |
| Carbonyl sulfide | 463-58-1 |
| Chlorobenzene | 108-90-7 |
| Cyclohexane | 110-82-7 |
| Chloroethane | 75-00-3 |
| Chloroform | 67-66-3 |
| Chloromethane | 74-87-3 |
| 1,2-Dibromoethane (EDB) | 106-93-4 |
| Decane | 124-18-5 |
| Dibromochloromethane | 124-48-1 |
| 1,2-Dichlorobenzene | 95-50-1 |
| 1,3-Dichlorobenzene | 541-73-1 |
| 1,4-Dichlorobenzene | 106-46-7 |
| Dichlorodifluoromethane | 75-71-8 |
| 1,1-Dichloroethane | 75-34-3 |
| 1,2-Dichloroethane | 107-06-2 |
| 1,1-Dichloroethene | 75-35-4 |
| cis-1,2-Dichloroethene | 156-59-2 |
| trans-1,2-Dichloroethene | 156-60-5 |
| 1,2-Dichloropropane | 78-87-5 |
| cis-1,3-Dichloropropene | 10061-01-5 |
| trans-1,3-Dichloropropene | 10061-02-6 |
| 1,2-Dichloro-1,1,2,2-tetrafluoroethane | 76-14-2 |
| Ethane | 74-84-0 |
| Ethanol | 64-17-5 |
| Ethylbenzene | 100-41-4 |
| 4-Ethyltoluene | 622-96-8 |
| Heptane | 142-82-5 |
| Hexane | 110-54-3 |
| Hexachlorobutadiene | 87-68-3 |
| 2-Hexanone | 591-78-6 |
| Octane | 111-65-9 |
| Methanol | 67-56-1 |
| Methylene Chloride | 75-09-2 |

| Analyte | CAS Number |
|---|---|
| 4-Methyl-2-pentanone (MIBK) | 108-10-1 |
| Naphthalene | 91-20-3 |
| Nonane | 111-84-2 |
| Pentane | 109-66-0 |
| Styrene | 100-42-5 |
| 1,1,2,2-Tetrachloroethane | 79-34-5 |
| Tetrachloroethene | 127-18-4 |
| Toluene | 108-88-3 |
| 1,2,4-Trichlorobenzene | 120-82-1 |
| 1,1,1-Trichloroethane | 71-55-6 |
| 1,1,2-Trichloroethane | 79-00-5 |
| Trichloroethene | 79-01-6 |
| Trichlorofluoromethane | 75-69-4 |
| 1,1,2-Trichloro-1,2,2-trifluoroethane | 76-13-1 |
| 1,2,4-Trimethylbenzene | 95-63-6 |
| 1,3,5-Trimethylbenzene | 108-67-8 |
| 2,2,4-Trimethylpentane | 540-84-1 |
| Vinyl acetate | 108-05-4 |
| Vinyl chloride | 75-01-4 |
| m,p-Xylene | 179601-23-1 |
| o-Xylene | 95-47-6 |

## Attachment B
## Aldehydes Required to be Included in Analysis
## (Suggested Modified EPA Method TO-11A)

| Analyte | CAS Number |
|---|---|
| 2,5-Dimethyl Benzaldehyde | 5779-94-2 |
| Acetaldehyde | 75-07-0 |
| Acetone | 67-64-1 |
| Acrolein | 107-02-8 |
| Benzaldehyde | 100-52-7 |
| Butyraldehyde | 123-72-8 |
| Crotonaldehyde | 4170-30-3 |
| Formaldehyde | 50-00-0 |
| Glutaraldehyde | 111-30-8 |
| Hexaldehyde | 66-25-1 |
| Isovaleraldehyde | 590-86-3 |
| m-Tolualdehyde | 620-23-5 |
| o-Tolualdehyde | 529-20-4 |
| Propionaldehyde | 123-38-6 |
| p-Tolualdehyde | 104-87-0 |
| n-Valeraldehyde | 110-62-3 |

## Attachment C
## PAH/Semi-volatile Organic Compounds Required to be Included in Analysis (Modified EPA Method TO-13A SIM or similar method as approved by CARB)

| Analyte | CAS Number |
|---|---|
| Acenaphthene | 83-32-9 |
| Acenaphthylene | 208-96-8 |
| Anthracene | 120-12-7 |
| Benzo[a]anthracene | 56-55-3 |
| Benzo[b]fluoranthene | 205-99-2 |
| Benzo[k]fluoranthene | 207-08-9 |
| Benzo[g,h,i]perylene | 191-24-2 |
| Benzo[a]pyrene | 50-32-8 |
| Chrysene | 218-01-9 |
| 2-Chloronaphthalene | 91-58-7 |
| Dibenz(a,h)anthracene | 53-70-3 |
| Fluoranthene | 206-44-0 |
| Fluorene | 86-73-7 |
| Indeno[1,2,3-cd]pyrene | 193-39-5 |
| 2-Methylnaphthalene | 91-57-6 |
| Naphthalene | 91-20-3 |
| Phenanthrene | 85-01-8 |
| Pyrene | 129-00-0 |

## Attachment D
## Other Compounds Required to be Included in Analysis

### Suggested Method ASTM D-1945/3588
### (Utilizing FID When Necessary to Achieve Detection Limit)

| Analyte | CAS Number |
|---|---|
| Oxygen | 7782-44-7 |
| Nitrogen | 7727-37-9 |
| Hydrogen | 1333-74-0 |
| Carbon Dioxide | 124-38-9 |
| Carbon Monoxide | 630-08-0 |
| Methane | 74-82-8 |
| Ethene | 74-85-1 |
| Propane | 74-98-6 |
| Propene | 115-07-1 |
| i-Butane | 75-28-5 |
| neo-Pentane | 463-82-1 |
| i-Pentane | 78-78-4 |
| Hexane Plus | |

### Suggested Method NIOSH 5523

| Analyte | CAS Number |
|---|---|
| Ethylene glycol | 107-21-1 |
| 1,3-Butylene glycol | 107-88-0 |
| Diethylene glycol | 111-46-6 |
| Propylene glycol | 57-55-6 |
| Tetraethylene glycol | 112-60-7 |
| Triethylene glycol | 112-27-6 |