

TEST PROTOCOL

EMISSION TEST PROGRAM

EPA ICR FOR PETROLEUM REFINERIES

SRU NO. 543 TGI STACK (EPN E-01-SCOT)

VALERO PORT ARTHUR REFINERY
PORT ARTHUR, TEXAS

PREPARED FOR:

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SECTION ONE

Introduction

ARI Environmental, Inc. (ARI) is submitting this test protocol to detail the test procedures to conduct an emission test program on the Sulfur Recovery Unit (SRU) No. 543 Tailgas Incinerator (TGI) stack, at the Valero Port Arthur Refinery (Valero) of The Premcor Refining Group Inc., a wholly owned subsidiary of Valero Energy, located in Port Arthur, Texas.

Testing will be conducted on the SRU No. 543 TGI stack in response to the USEPA Section 114 Information Collection Request (ICR) for Petroleum Refineries. The specific pollutants, test run duration and units of measure that will be determined are presented in Table 1-1. The parameters and associated test methods are presented in Table 1-2.

Included in this test protocol are sections detailing the testing and analytical procedures, test schedule, data reduction and report format, and ARI's related experience in stack emission and control equipment efficiency testing.

This test program and field team will be managed by Mr. Dan Fitzgerald.

DISCLAIMER: This test protocol has been developed based upon information and USEPA guidance as it exists at the time of preparation. Please note that methodology and analytical approach may change without notice due to USEPA ICR updates.



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TABLE 1-1. POLLUTANTS, TEST RUN DURATION AND UNITS OF MEASURE

Group ¹	Pollutant	Test Run Duration (hours) ²	Units of Measure
A1	Speciated Volatile Organic Hazardous Air Pollutants (HAP)	1	lb/hr, µg/dscm
A2	Speciated Semi-Volatile Organic HAP	4	lb/hr, µg/dscm
A1	Aldehydes	1	lb/hr, µg/dscm
A3	Total Hydrocarbons (THC)	1	lb/hr, ppmv db
A3	Methane, Ethane	1	lb/hr, ppmv db
A3	Carbon Monoxide (CO)	1	lb/hr, ppmv db
F	Hydrogen Sulfide (H ₂ S), Carbonyl Sulfide (COS) and Carbon Disulfide (CS ₂)	3	lb/hr, ppmv db
	Total Reduced Sulfur (TRS) compounds	3	ppmv db
A, F	Flow Oxygen (O ₂), Carbon Dioxide (CO ₂) Moisture	Conducted simultaneously with the sampling in each group.	acfm, scfm, dscfm % by volume db % by volume

¹Simultaneous sampling will be conducted for all pollutants in each group.

²Three test runs will be conducted for each pollutant.

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TABLE 1-2. POLLUTANTS AND TEST METHODS

Group	Pollutants	Test Methods	Isokinetic Sampling
A1	Speciated Volatile Organic HAP	USEPA Methods 18 and 308	No
A2	Speciated Semi-Volatile Organic HAP	SW-846 Method 0010 with SW-846 Method 8270C/D analytical finish. At least 4 m ³ will be collected per run.	Yes
A1	Aldehydes	SW-846 Method 0011 with SW-846 Method 8315A. A minimum volume of 1.3 m ³ will be collected.	Yes
A3	THC	USEPA Method 25A	No
A3	CO	USEPA Method 10	No
A3	Methane, Ethane	USEPA Method 18	No
F	H ₂ S, COS and CS ₂	USEPA Method 15: A minimum of 16 samples during a period of 3 to 6 hours per run	No
F	TRS	USEPA Method 16A: A minimum of 3-hour sample time per run	No

For the Groups A1 and A2 components, ARI proposes to subcontract the analytical to ALS Environmental located in Burlington, Ontario. Groups A3 and F will be performed by ARI either while onsite or at our laboratory located in Pasadena, Texas. ALS Environmental has quoted analytical turnaround times of 21 to 28 days upon sample receipt at their laboratory.

SECTION TWO

Testing and Analytical Procedures

2.1 OVERVIEW

It is proposed to conduct an emission test program on the SRU No. 543 TGI stack at the Valero Port Arthur Refinery located in Port Arthur, Texas. Testing will be conducted in response to the USEPA Section 114 ICR for Petroleum Refineries. Three (3) test runs will be conducted at the SRU No. 543 TGI stack for all pollutants. The test run durations are shown in Table 1-1. The test methods are summarized in Table 1-2.

2.2 METHODOLOGY

Test methods will follow the Code of Federal Regulations, Title 40, Part 60 (40 CFR 60), Appendix A, USEPA Methods 1-4, 10, 15, 16A, 18 and 25A; 40 CFR 51, Appendix M, USEPA Method 205; 40 CFR 63, Appendix A, USEPA Method 308; SW-846 Methods 0010, 0011, 8270C/D and 8315A; and the Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods.

2.2.1 Sampling Location (USEPA Method 1)

The sampling point locations for the determination of gas velocity and volume flow rate will be determined following the procedural requirements as detailed in USEPA Method 1. Sampling will be conducted at the SRU No. 543 TGI stack in the four (4) sampling ports provided in the 150-inch diameter duct. The sample ports are located approximately 460 inches (3.1 duct diameters) upstream and 688 inches downstream (4.6 duct diameters) from the nearest flow disturbances. Twenty-four (24) traverse points will be used to sample the cross-sectional area of the stack.

2.2.2 Flue Gas Volumetric Flow Rate (USEPA Method 2)

Gas velocity and volumetric flow rate will be determined following USEPA Method 2. Velocity head measurements will be performed using a Type S pitot tube and Dwyer inclined 0 – 10-in. water manometer. Temperature measurements will be conducted using a Chromel-Alumel thermocouple connected to a digital direct read-out potentiometer.

2.2.3 Oxygen, Carbon Dioxide and Carbon Monoxide (USEPA Methods 3A and 10)

O₂ and CO₂ concentrations will be determined following USEPA Method 3A procedures using ARI's Servomex, Inc. Model 1440C combination paramagnetic O₂ and non-dispersive infrared CO₂ analyzer. CO sampling will follow USEPA Method 10 procedures using ARI's Thermo Environmental, Inc. Model 48i gas filter correlation non-dispersive infrared CO analyzer.

As shown in Figure 2-1, ARI's sampling system will consist of a heated probe with in-stack filter followed by a calibration tee assembly. The probe system will be connected to a heated Teflon sampling line that transports the gas sample through an ice-cooled condenser and an electronic chiller to remove moisture. The dry sample gas is then transported to a manifold system by a Teflon lined sample pump and Teflon sample line. The manifold is connected with sample gas intake lines for ARI's O₂, CO₂ and CO analyzers.

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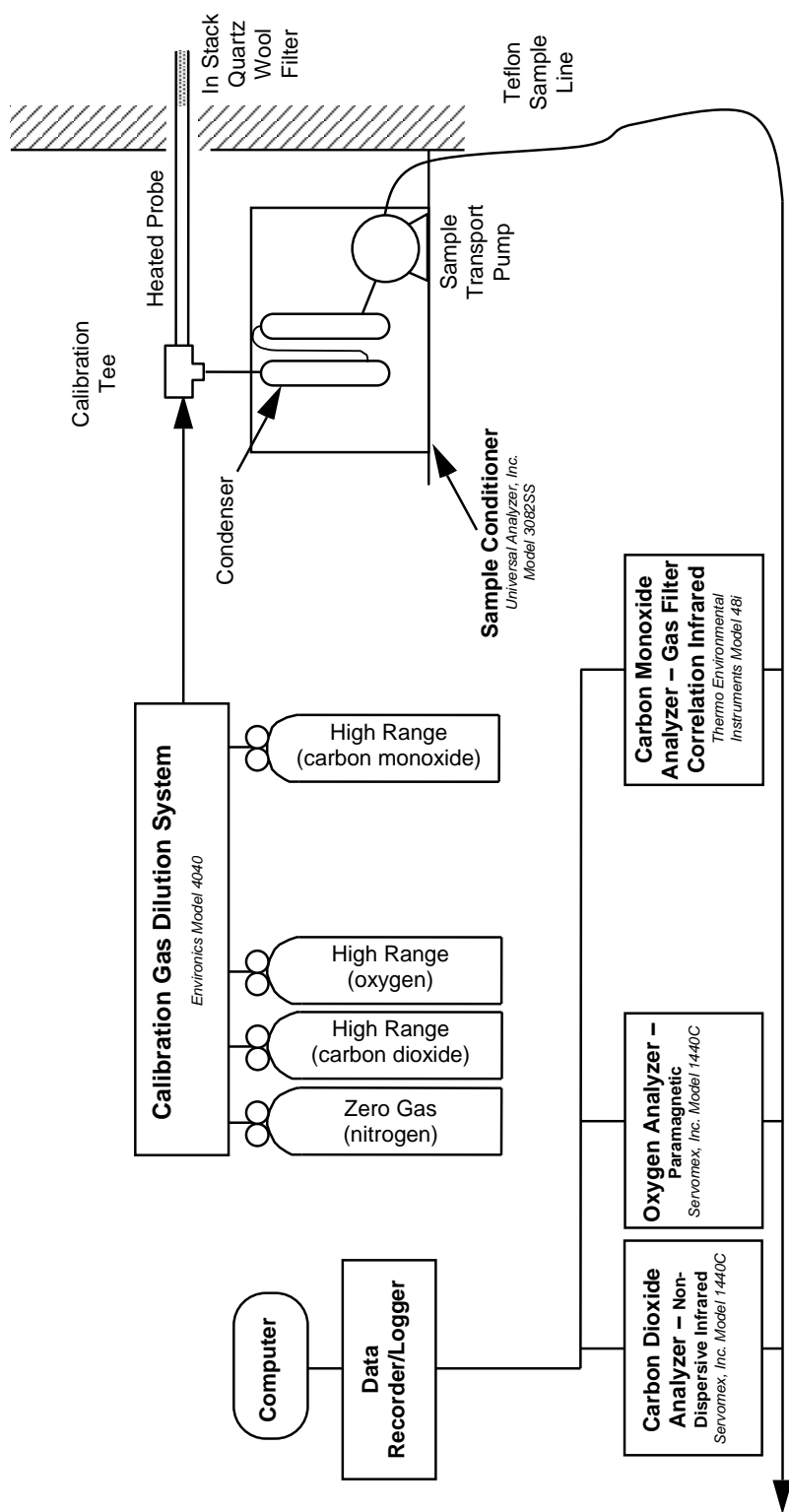


FIGURE 2-1. ARI REFERENCE METHOD CO₂, O₂ AND CO SAMPLING SYSTEM

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ARI's monitors will be calibrated with applicable zero, mid-range and high-range gases as specified in the applicable USEPA methods. The calibration gases will be generated from Protocol 1 calibration gases using an Environics Model 4040 Gas Dilution System. The gases will meet the calibration gas protocols as specified in USEPA Method 7E, Section 7.1.

Response time, calibration error and measurement system bias tests will be performed prior to testing and a pre/post calibration drift test will be conducted after each test repetition on each monitor. The average zero and calibration drift values obtained during each test run on the monitor will be used to correct each monitor's raw data for instrument zero and drift for each respective test run.

The monitor data will be collected at 15-second intervals and one-minute averages will be calculated by ARI's data acquisition system consisting of an Omega OMB-DAQ-56 data acquisition module connected to a computer for digital data archiving and data reduction.

2.2.4 Flue Gas Moisture Content (USEPA Method 4)

The stack gas moisture content will be determined following USEPA Method 4. This method will be performed as part of the pollutant sampling trains. Moisture will be collected in a series of chilled impingers containing methodology specific liquids and silica gel. A dry gas meter to determine the sample volume will follow the impingers. The amount of volume gain in the water impingers and weight gain in the silica gel impinger will be used to calculate the moisture content. Figure 2-2 presents a schematic of the standalone moisture train that is not combined with another sampling system.

2.2.5 COS, CS₂ and H₂S (USEPA Method 15)

Determination of COS, CS₂ and H₂S will be conducted in accordance with USEPA Method 15 using a gas chromatograph (GC) for separation of sulfur compounds and measurement by a flame photometric detector (FPD).

Modifications and improvements to USEPA Method 15 during the testing will include the following:

1. No sample dilution is required (GC range ~500 ppm)
2. USEPA Protocol 1 calibration gases will be used to calibrate the GC (no permeation tubes used)

The gas sampling system will consist of a ¼-inch stainless steel probe connected to a Teflon sampling line. The exhaust gas will then be conveyed through a series of Teflon impingers located on the sampling platform containing a citrate buffer solution to remove most of the sulfur dioxide (SO₂) from the sample stream.

A Teflon lined sample pump will transport the sample in ¼-inch ID Teflon tubing to the ARI mobile laboratory. The sample will be run to a manifold system at a flow rate of nominally 3-5 liters per minute from which a sample is introduced to the GC-FPD.

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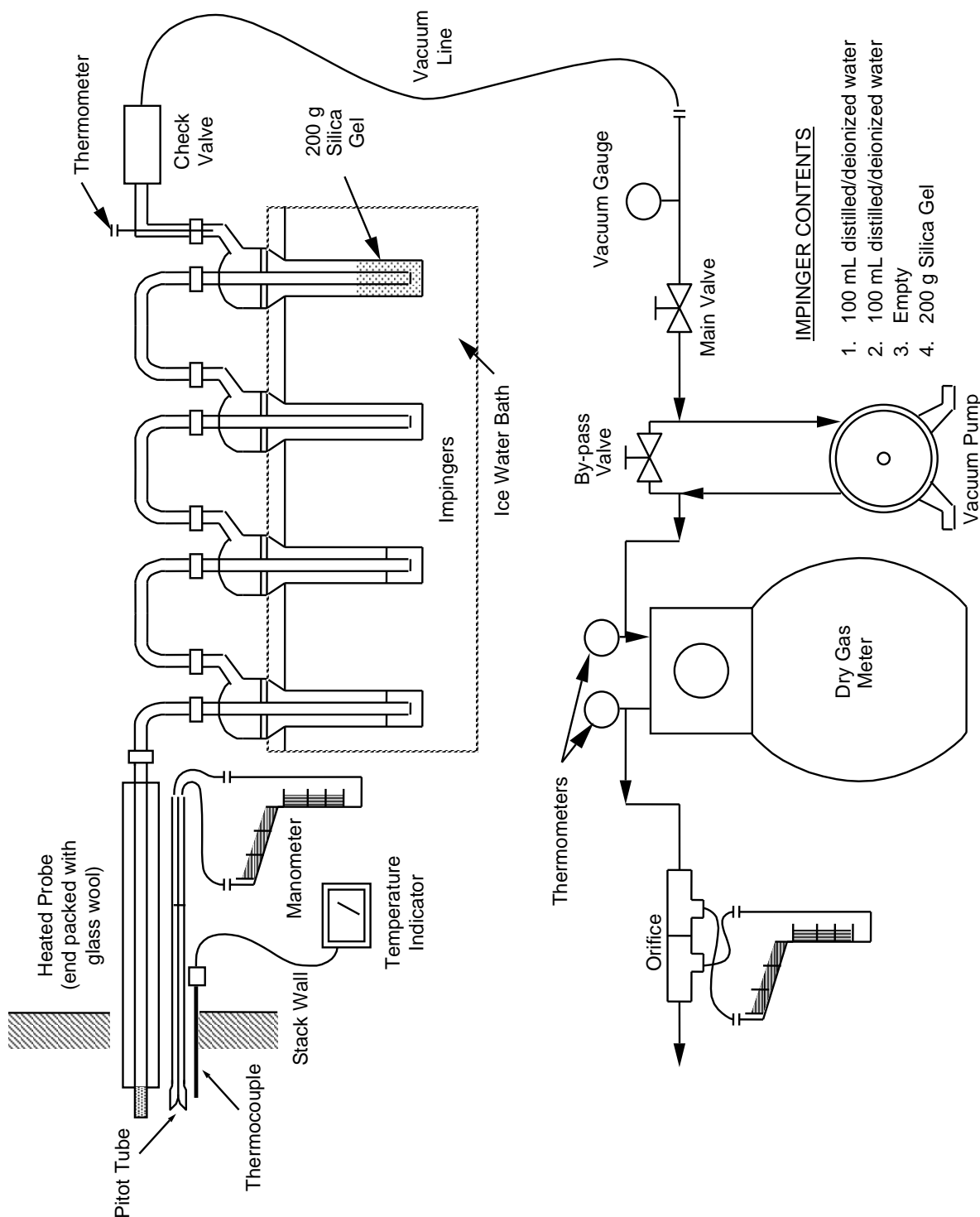


FIGURE 2-2. USEPA METHOD 4 SAMPLING TRAIN (MOISTURE)



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The GC-FPD system will consist of an SRI Model 9300B field GC containing a heated gas sampling valve, column oven and detector. A computer based integrator utilizing Peak Simple software will be used for data acquisition and integration. Linear regressions of the square root of the area counts will be used to calculate the calibration curves. A line loss test will be conducted prior to the start of the test program.

The GC-FPD will be calibrated with USEPA Protocol 1 gas standards. The gas standards will be generated using an Environics Model 4040 Gas Dilution System. During each 180-minute test run, there will be at least 16 injections to the GC-FPD.

2.2.6 TRS (USEPA Method 16A)

The determination of TRS will be conducted in accordance with USEPA Method 16A. This method extracts an integrated sample from the stack and removes SO₂ using a citrate buffer scrubbing solution. TRS is then oxidized in a combustion tube to SO₂ and collected as sulfate in the hydrogen peroxide (H₂O₂) impinger assembly. The sample collection assembly is followed by a dry gas metering system. The mass of TRS as SO₂ collected will be measured by the analytical procedures contained in USEPA Method 6 using a barium-thorin titration. The major components of the sampling system are described below:

2.2.6.1 Sampling Apparatus

Probe – ¼-in. quartz tubing.

Particulate Filter – 50 millimeter (mm) Teflon filter holder containing a 1-2 µm porosity Teflon filter. The filter holder will be heated to a sufficient temperature that will prevent condensation of moisture (>250°F).

SO₂ Scrubber – Three 300 milliliter (mL) Teflon segmented impingers connected in series by thick walled Teflon tubing. The first two impingers will contain 100 mL of citrate buffer and the third impinger will initially be empty. The tips of the impinger stems that are below the solution level will have an inner diameter no greater than ¼-in.

Combustion Tube – Quartz glass tube with a 12-in. long, 1-in. expanded diameter combustion chamber with ¼-in. connections on both ends.

Furnace – Capable of housing and heating the combustion tube to 1,472°F ±180°F.

Peroxide Impingers – Four (4) midjet impingers connected in series. The first two impingers will contain 20 mL of 3% H₂O₂, the third impinger will initially be empty and the fourth impinger will contain silica gel.

Dry Gas Meter – Capable of measuring gas volume at a sample rate of 2 LPM at an accuracy of 2%.



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2.2.6.2 Sampling Procedures

The sampling system is assembled with the probe connected to the heated filter followed by the citrate buffer SO₂ scrubber, then to the heater combustion tube followed by the H₂O₂ impingers and metering system. The appropriate volumes of solutions are placed in the SO₂ scrubber and H₂O₂ impingers. The citrate buffer is initially disconnected at the exit end and is conditioned by pulling stack gas through the system at 2 LPM for 10 minutes. After the initial conditioning period, the citrate buffer is reconnected to the entrance to the combustion tube and the sampling system is leak-checked. Following a successful leak-check, the system is ready to begin sampling stack gas at a rate of 2 LPM for 180 minutes.

2.2.6.3 Sample Recovery Procedures

After the 180-minute sampling period is over and the sampling system successfully passes a post-test leak check, the peroxide impingers are disconnected and recovered. The contents of the first three impingers are collected into a leak-free polyethylene jar and a subsequent rinse of the impingers and connecting glassware are also placed in the sample jar. The fluid level is marked and the impingers are sealed and identified.

After completion of each 180-minute test run, a system performance check is conducted to validate the test run and the sample train components and procedure. This will involve sampling a known concentration of H₂S prior to cleaning the components upstream of the peroxide impingers and before recharging the citrate buffer solution. A 30-minute sample will be collected at a rate of 2.5 LPM and the H₂O₂ impingers will be recovered and analyzed in the same manner as the 180-minute stack samples.

2.2.6.4 Analytical Procedures

Analysis of each sample will be conducted by ARI personnel while onsite by using the barium-thorin titration procedures described in USEPA Method 6.

2.2.7 Methane and Ethane (USEPA Method 18)

Methane and ethane will be measured in conjunction with the THC (USEPA Method 25A) procedures. Tedlar bag samples will be collected concurrently and analyzed by calibration procedures described in USEPA Method 18.

Specifically, the concentrations will be measured by flame ionization detection with separation by gas chromatography (GC-FID). The GC-FID will be calibrated by triplicate injections of cylinder gas standards to calculate a 4-point calibration curve. Since methane and ethane are non-reactive and considered stable in the bags, procedures will not be conducted to determine the percent recovery of methane or ethane in the bags.

Calibration gases will be diluted from USEPA Protocol 1 high concentration standards. Dilution will be performed using ARI's Environics Model 4040 Gas Dilution System. The dilution system will be verified onsite before the start of testing following procedures described in USEPA Method 205.



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2.2.8 Speciated Volatile Organic HAP (USEPA Method 18)

Volatile organic HAP sampling and analysis will be conducted following the Method 18 Midget Impinger Method approved by USEPA and referenced on the Refinery ICR Website (FAQ Test-029) as an alternate method to determine the stack gas concentrations and emission rates of target volatile analytes listed in Table 1.3 of Component 4 of the ICR. This method utilizes a midget impinger train with chilled ultrapure grade methanol as the volatiles collection media (see Attachment A).

The test itself will consist of three one-hour sampling runs and will be conducted simultaneously with the semi-volatile organic HAP sampling. Each of the sampling runs will be conducted following USEPA Method 18 criteria for sorbent train sampling which requires that two co-located sampling trains be operated simultaneously. The co-located trains will be spiked with both "labeled" and "native spikes" covering a specific list of recovery surrogates included in the refinery ICR Component 4 document. The purpose of this spiking is to satisfy the quality assurance recovery requirements set forth by the method and to demonstrate the quality of the measurement data. The recovery surrogates that will be spiked into the co-located trains will include the following:

Labeled Spikes (added to each of the co-located trains):

1,3-Butadiene-d6	2,2,4-Trimethylpentane-d18
Pentane-d12	2-Nitropropane-d6
MTBE-d12	1,2-Dibromoethane-d4
n-Hexane-d14	Ethylbenzene-d10
Acrylonitrile-d3	Styrene-d8
Benzene-d6	Nitrobenzene-d5

Native Spikes (added to the co-located spiked train only):

Acrolein
Acetonitrile
Toluene
Trichloroethene
Methyl *iso*-Butyl Ketone

2.2.8.1 Sampling Apparatus

Each of the two co-located sampling trains will consist of the following components:

Probe - Heated stainless steel probe with quartz liner.

Coil Condenser - Borosilicate glass condenser to cool the sample gas stream prior to entering the impinger train.

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Impinger Train - Five borosilicate glass midget impingers with the first impinger acting as a moisture and condensables knockout and fitted with a shortened impinger tip. The second, third, and fourth impingers will each contain an ultrapure grade (purge and trap grade) of methanol (10-20 mL each) with each impinger fitted with a tapered or fritted insert. The fifth impinger will contain approximately 25 grams of silica gel to remove the final traces of moisture from the gas sample.

Meter Console - A VOST type meter console will be used to control the sampling rate through the impinger train and monitor the temperature of the sampling train components. The meter console itself will contain a dry gas meter to measure the volume of gas sampled. The gas meter will have an accuracy of $\pm 1\%$.

2.2.8.2 Sampling Procedures

Sampling Train Glassware Preparation

The sampling train glassware will be pre-cleaned, thoroughly rinsed with ultrapure grade methanol, baked in an oven at 100°C for two hours, cooled, sealed and stored separately from other reagents and other equipment to avoid contamination prior to assembly of the sampling train.

Recovery Surrogate Spiking of Impinger Train

The co-located sampling trains will be assembled prior to charging the impingers with methanol. The co-located trains will both be field spiked with the “labeled” spikes and the spiked train will also be spiked with the “native” spikes using the surrogate recovery standards prepared by the analytical laboratory. The contents of the prepared spikes will be charged directly into impinger #2 of the sampling train.

Sampling Train Operation

A leak check of the sampling train will be performed before and after each sampling run at near 10 inches of mercury and will be performed such that exposure of sampling train components to possible ambient air contaminants will be avoided.

Following the leak check and prior to sampling, the sampling probe will be heated to a temperature to prevent the condensation of organics and water vapor (280° to 302° F). The first four impingers of the sampling train will be placed into a dry ice/methanol water bath and allowed to cool the impinger absorbing solutions prior to the start of sampling. Under these conditions, the target analytes of interest are efficiently trapped and dissolved in the methanol and stability of the samples is assured prior to analysis. Ice water will be circulated through the pre-impinger coil condenser to ensure that the first knockout impinger effectively collects sample gas condensate and low boiling organic components.



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The probe will be introduced into the stack and located either close to the centroid or greater than 3-feet from the inner wall of the stack cross-sectional plane. Sampling will be conducted at a constant rate of 0.25 liters/minute during each sampling run to collect a nominal 20 L sample volume. Sampling train flow rate, temperature, and gas volume data will be recorded at five-minute intervals throughout each sampling run. Following completion of the run, the sampling train will be leak checked following the pretest leak check procedure.

2.2.8.3 Sample Recovery

Sample recovery from each of the co-located sampling trains will be conducted as follows:

Container No. 1 - The contents of midjet impingers #1 and #2 will be combined, rinsed with a small quantity of methanol, and placed in a labeled 40 mL VOA vial. The probe, coil condenser and connecting glassware and tubing to the first impinger will be rinsed with three small volumes of methanol and added to the Container No. 1 (VOA vial). The vial will be labeled as Method 18 1st and 2nd Methanol Impinger Composite.

Container No. 2 - The contents of midjet impinger #3 and rinse will be placed in a separate 40 mL VOA vial and labeled as Method 18 3rd Methanol Impinger. This fraction will be analyzed separately from the first fraction.

Container No. 3 - The contents of midjet impinger #4 and rinse will be placed in a separate 40 mL VOA vial and labeled as Method 18 4th Methanol Impinger. This fraction will be analyzed separately from the other fractions.

Following sample recovery, the methanol sample vials will be placed in separate sealable poly bags and stored in coolers on dry ice prior to and during shipment of all samples to the analytical laboratory.

Blank Train and Trip Blanks (Quality Control Samples)

A train blank set of Method 18 samples and a methanol trip blank will be collected one time during each source location.

During one of the sampling runs, a complete blank train will be set up in the same manner as the sample trains. The methanol will remain in the identical train for the same length of time as the duration of the sampling run. Beginning and end leak checks will be performed and the probe will be heated to temperature. The blank train samples will be recovered in the same manner as those for the stack sampling runs.

Additionally, once for each test, a field spike will be prepared for each of the two spiking standards (native and labeled spikes) by adding the contents of each spiking ampoule to a VOA vial containing 5 to 10 ml of purge and trap grade methanol. The vial is then filled with additional methanol to reduce headspace. These field spikes will be QC samples to provide additional baseline data for the recovery study.

2.2.8.4 Analytical Procedures

Analysis of the collected stack run samples and one methanol trip blank sample per source will be performed by ALS Environmental Laboratories following SW-846 Methods 5030C/8260B employing purge and trap GC/MS procedures.



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Sample volumes of the methanol sorbent for the purge and trap analysis procedure will be adjusted in order to achieve a low end target analysis concentration in the stack gas stream of 0.1 ppmv.

All of the quality assurance and control requirements set forth in USEPA Method 18 for sorbent train sampling and analysis for VOC will be followed, where applicable.

2.2.9 Total Hydrocarbons (USEPA Method 25A)

THC sampling will be conducted in accordance with USEPA Method 25A using a VIG Industries hydrocarbon analyzer equipped with a heated FID.

The sample delivery system will consist of a stainless steel probe, filter and calibration tee (on the end of the probe) connected to a heated 250°F Teflon sampling line. The sampling lines connect directly into the analyzers located in ARI's monitoring trailer. The THC analyzer is internally heated to keep the sample gas stream above its dew point (see Figure 2-3).

The analyzer will be calibrated with applicable zero, low-range, mid-range and high-range gases as specified in USEPA Method 25A. The calibration gases will be generated from Protocol 1 calibration standards using an Environics Model 4040 Gas Dilution System. The dilution system will be verified on-site in strict accordance with USEPA Method 205. The gases will meet the calibration gas protocols specified in USEPA Method 7E, Section 7.1.

A calibration error test and measurement system bias test will be performed prior to testing and a post calibration drift test will be done on the monitor. The average zero and calibration drift values will be used to correct the raw monitor data for each respective test run.

The monitor's data will be collected at 15-second intervals by ARI's data acquisition system which consists of an Omega OMB-DAQ-56 datalogger connected to a computer for digital data archiving and data reduction. DaqViewXL and Excel spreadsheet computer software will be used for calculation of emission rates.

2.2.10 Gas Dilution System Verification (USEPA Method 205)

All applicable calibration gases will be certified by USEPA Protocol 1 procedures. All diluted calibration standards will be prepared using an Environics Model 4040 Gas Dilution System that will be verified by a field evaluation prior to testing following the requirements of USEPA Method 205 (40 CFR 51, Appendix M).

ARI's Servomex Model 1440C O₂ analyzer will be initially calibrated following USEPA Method 3A procedures. After the calibration procedure is complete, diluted low and mid-range standards and a mid-range EPA Protocol 1 standard will be alternately introduced in triplicate and an average instrument response will be calculated for each standard. No single response may differ by more than $\pm 2\%$ from the average response for each standard. The difference between the instrument average and the predicted concentration must be less than $\pm 2\%$ for each diluted standard. The difference between the certified gas concentration and the average instrument response for the mid-range EPA Protocol 1 standard must be less than $\pm 2\%$.

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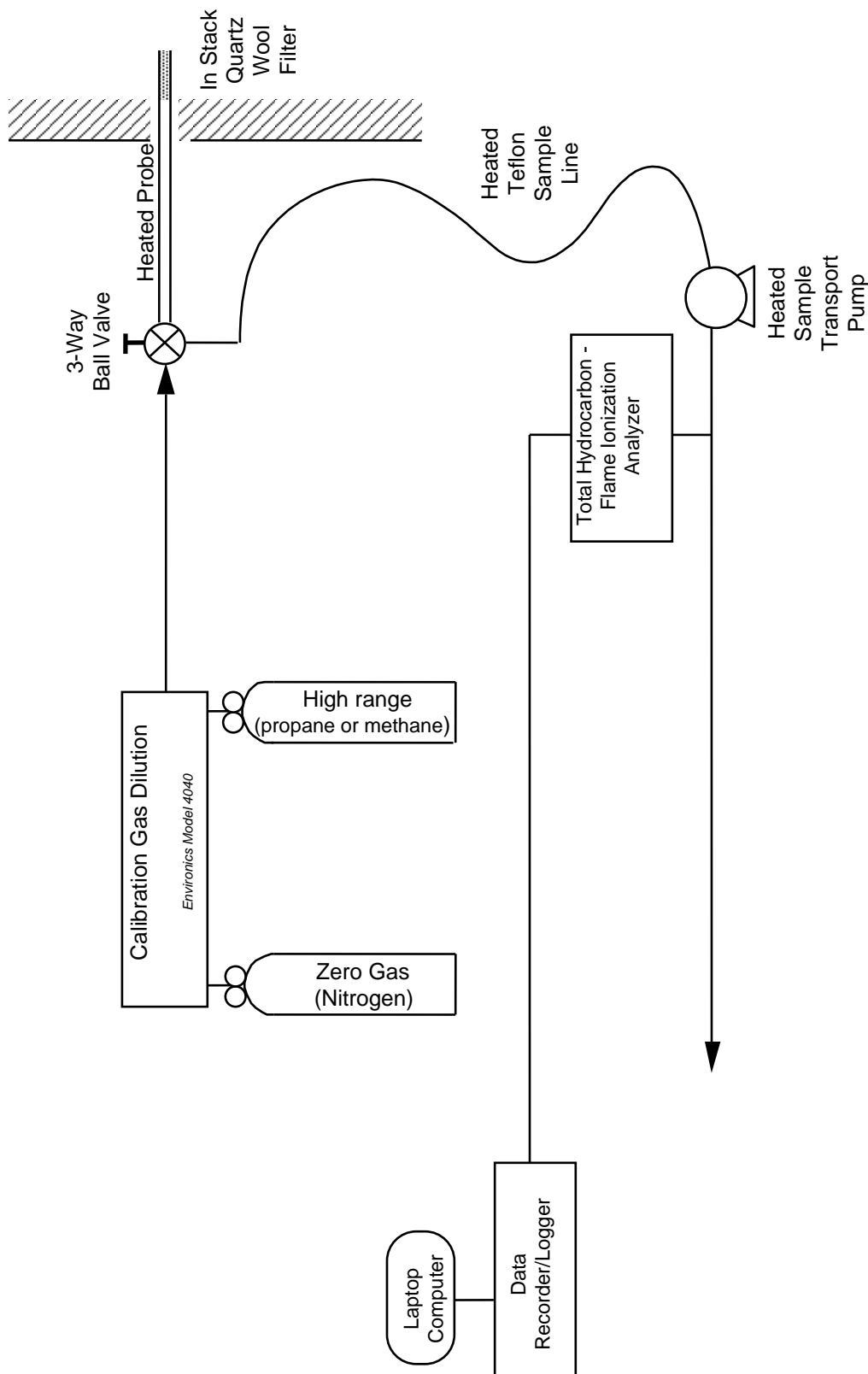


FIGURE 2-3. USEPA METHOD 25A - THC SAMPLING SYSTEM



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2.2.11 Methanol Determination (USEPA Methods 308/18)

Methanol concentration and emission rate will be determined following the basic principles of USEPA Method 308. Since the refinery ICR volatile organic HAP sampling requirements include surrogate spiking and recovery determination, the USEPA Method 308 test procedure will include the addition of a co-located sampling train spiked with the target analyte (methanol) and operated simultaneously with the stack gas sampling train. This will satisfy the ICR volatile organic HAP surrogate spiking and recovery requirement.

2.2.11.1 Sampling Apparatus

As shown in Figure 2-4, each of the co-located sampling trains will consist of the following components:

Probe - Heated stainless steel or quartz lined probe.

Teflon Tube - Connecting the probe to the absorbing solution/condensate impinger.

Impinger - Borosilicate glass impinger with tapered insert to collect moisture and condensable organics.

Sorbent Tube - Two section silica gel trap to collect non-condensable methanol fraction.

Pump - To transport gas sample through sampling train.

Needle Valve - To control gas sample flow rate through the sampling train.

Meter Console - A VOST type meter console will be used to control the sampling rate through the impinger train and monitor the temperature of the sampling train components. The meter console itself will contain a dry gas meter to measure the volume of gas sampled. The gas meter will have an accuracy of $\pm 1\%$.

The unspiked sampling train will include one midget impinger charged with 20 mL of ultrapure deionized water.

The spiked train will include one midget impinger charged with 20 mL of laboratory prepared spiking solution for the recovery determination. The spiked train will also include a two-section silica gel sorbent tube spiked with a known mass of ultra pure methanol into the first section for the recovery determination.

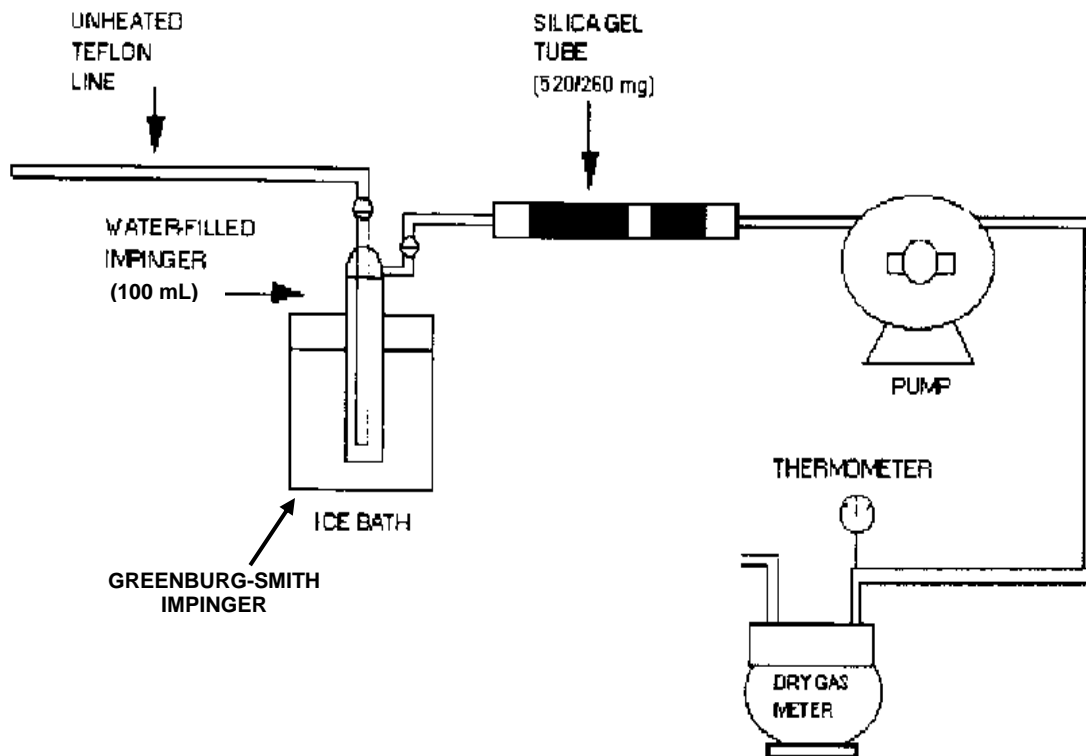
2.2.11.2 Sampling Procedures

Prior to the start of sampling, each of the sampling trains will be leak checked at 10 inches of Hg. Acceptable leak rate is $\leq 2\%$ of the average sampling rate. Following the leak check, the impinger will be immersed in an ice water bath and the sample probe will be positioned in the centroid of the stack. The sample probe will be purged and sampling will begin with the sample rate adjusted to a selected flow rate in the range of 200 to 1000 mL/minute (dependent upon the anticipated methanol concentration in the stack and the detection limit required). Sample train flow rate and temperature data will be recorded at five-minute intervals throughout the duration of the run. Following completion of the run, a post test leak check will be performed in the same manner as that conducted prior to the start of the run.

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FIGURE 2-4. USEPA METHOD 308 SAMPLING SYSTEM





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2.2.11.3 Sample Recovery Procedures

Sample recovery from each of the two co-located trains will be conducted as follows:

Container #1 - The impinger absorbing solution and water rinse of the impinger and upstream sample tubing will be stored in a labeled and sealed 40 mL VOA vial and stored in a cooler with ice packs.

Silica Gel Sorbent Tube - The sorbent tube will be capped, labeled, and stored in a cooler with cold packs.

Blanks - A methanol field blank and a sorbent tube blank will be collected once for each source tested.

2.2.11.4 Analytical Procedures

At ARI's laboratory, the collected samples will be analyzed using an SRI Model 8610 gas chromatograph equipped with a FID following USEPA Method 308 procedures to determine the methanol concentration.

Calibration of the gas chromatograph will be performed using liquid standards prepared in the same impinger absorbing solution matrix as well as standards prepared in the sorbent tube desorbing solution. The samples will be analyzed and target analyte recoveries will be determined to meet the QA recovery requirements set forth in USEPA Method 18. Analyte recovery must be within the 70 to 130% R value range allowed by the method and the R value must be applied to the analytical results.

2.2.12 Speciated Semi-Volatile Organic HAP (SW-846 Method 0010)

Sampling in accordance with SW-846 Method 0010 will be conducted for the following target analytes:

Acenaphthene	Dimethylaminobenzene
Acenaphthylene	7,12-Dimethylbenz(a)anthracene
Aniline	3,3-Dimethylbenzidine
Anthracene	α , α -Dimethylphenethylamine
Benzidine	2,4-Dimethylphenol
Benz[a]anthracene	Fluoranthene
Benzo[b]fluoranthene	Fluorene
Benzo[k]fluoranthene	Indeno(1,2,3-cd)pyrene
Benzo[g,h,i]perylene	Isophorone
Benzo[a]pyrene	3-Methylcholanthrene
Benzo[e]pyrene	2-Methylnaphthalene
Biphenyl	Naphthalene
Cresol (mixed isomers)	Perylene
Chrysene	Phenanthrene
Dibenz[a,h]anthracene	Phenol
Dibenzofuran	1,4-Phenylenediamine
Dibenzo(a,e)pyrene	Pyrene
3,3-Dimethoxybenzidine	o-Toluidine

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The samples will be withdrawn isokinetically from the stack location through a heated particulate filter followed by a condenser, a XAD-2 resin sorbent trap and a series of chilled impingers.

2.2.12.1 Sampling Apparatus

The sampling train is an Apex Instruments Modified Method 5 sampling train (see Figure 2-5). The major components are described below:

Nozzle - Borosilicate glass with sharp tapered leading edge.

Probe – Stainless steel with borosilicate glass liner and attached pitot tube and stack temperature thermocouple.

Apex Sample Box - Containing Pyrex glass filter holder, glass fiber filter, a water jacketed sample chiller, a sorbent trap containing XAD-2 resin, five Greenburg-Smith impingers and the connecting glassware.

Apex Control Module – (per USEPA Method 5 specifications) containing pump, heat controllers and inclined-vertical oil gauge manometer.

The sample adsorbent traps and filters will be cleaned and prepared by the laboratory following SW-846 Method 0010 procedures. ARI will clean all sampling train glassware to pesticide analytical requirements using procedures outlined in Section 3A of the “Manual of Analytical Methods for the Analysis of Pesticide in Human and Environmental Samples”.

The sample train is assembled as follows:

1. A glass nozzle is selected and attached to the probe.
2. A pre-weighed, pre-cleaned glass fiber filter is placed in the filter holder and its number recorded on the data sheets.
3. The water jacket sample condenser and sorbent trap containing 50 grams of XAD-2 resin are placed in series after the filter holder.
4. The back half of the train will consist of five impingers. The first impinger is assembled empty. The second and third impingers will contain 100 mL of HPLC grade water. The fourth impinger is assembled empty. The fifth impinger will contain 200 grams of silica gel.

All glassware, filter media and chemicals will be prepared to pesticide grade cleanliness using solvent rinse procedures as specified in the method.

5. The sampling train will be assembled on-site in ARI's monitoring trailer.

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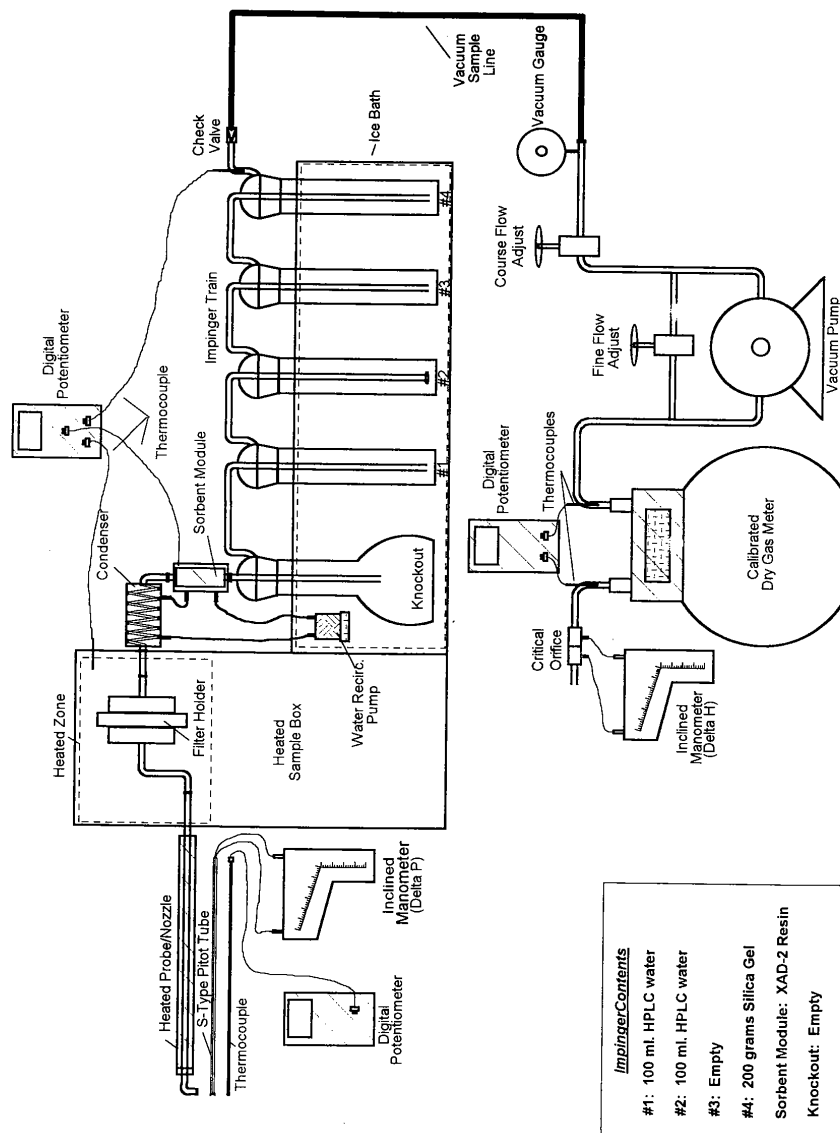


FIGURE 2-5. SW-846 METHOD 0010 SAMPLING TRAIN



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2.2.12.2 Sampling Procedures

The sampling train is leak checked prior to sampling using the following procedures:

1. The pump is started.
2. The course flow adjustment valve is opened.
3. Flow through the dry gas meter is checked.
4. The probe inlet is plugged.
5. The fine flow adjustment valve is adjusted so that the vacuum gauge reads 15 in. Hg.
6. If the flow exceeds .02 ACFM, the pump is shut off and all connections are rechecked for tightness and the leak test procedure is repeated until acceptable results are obtained.

The pitot tube assembly is leak checked using the following procedures:

1. A positive (or negative) pressure of greater than 3 inches of water is created in the pitot line to be checked.
2. The line is plugged to hold the pressure, and the manometer is monitored to watch for any change in the reading.
3. If the reading changes, the system is rechecked for leaks and the leak check procedure is repeated until no leaks are present.

Crushed ice is added to the impinger compartment and the sample case is moved into position outside the first port to be sampled. When the filter holder assembly is properly heated, the nozzle is uncapped and the probe introduced into the stack to the first sampling point. The dry gas meter reading is recorded and sampling is started. At each point, a pitot reading is made and the sampling rate adjusted using calculations based on preliminary temperature, pressure and estimated moisture. The sorbent traps are maintained below 68°F to insure XAD collection efficiency during testing. When sampling at the last point in the port is complete, the pump is turned off and the probe is carefully removed from that port.

A final leak test is performed on the sampling train, as previously described. The umbilical cord is disconnected, and the sample case and probe are then disassembled.

2.2.12.3 Sample Recovery Procedures

Upon completion of each test run and final leak check, the following sampling train clean-up procedure will be performed:

Container 1 - The filter is removed from its holder and is placed and sealed in a glass Petri dish.



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Container 2 - All loose particulate matter and rinse washings from all sample-exposed surfaces preceding the filter paper are placed in this container and sealed. The probe, nozzle and connecting heated Teflon line are scrubbed with a stiff Teflon brush and rinsed with deionized water. The final level of liquid is marked on the bottle.

Container 3 - The contents of impingers 1, 2, 3 and 4 are measured for volume and then placed in Container 3. The total volume is measured to the closest ± 1 mL and the liquid level is marked on the outside of the bottle.

Container 4 - The silica gel from impinger 5 is placed in Container 4.

Containers 5 & 6 - The sorbent traps are sealed with Teflon tape and glass ends. The traps will be refrigerated in ARI's monitoring trailer.

Blanks - During testing, an acetone blank, toluene blank, XAD-2 resin blank and glass fiber filter blank will be collected and placed into respective glass bottles with Teflon lined lids for analysis.

2.2.12.4 Analytical Procedures

After all chain of custody forms are completed, the samples will be shipped to the laboratory for analysis in accordance with SW-846 Method 0010 and 8270C or D. The samples will be stored in ice chests containing coolant packs.

2.2.13 Aldehydes (SW-846 Method 0011)

Sampling for aldehydes (formaldehyde, acetaldehyde, propanal) will be conducted in accordance with SW-846 Method 0011 using an Apex Instruments, Inc. sampling train as shown in Figure 2-6. The impinger catch will be analyzed for aldehydes in accordance with SW-846 Method 8315A procedures.

2.2.13.1 Sampling Apparatus

The aldehydes sampling train will meet design specifications established by the USEPA. Assembled by ARI personnel, it will consist of the following:

Nozzle - Quartz with sharp, tapered, leading edge and accurately measured round opening.

Probe - Quartz with a heating system capable of maintaining a gas temperature of $248^{\circ}\text{F} \pm 25^{\circ}\text{F}$ at the exit end during sampling.

Pitot Tube - A Type-S pitot tube that meets all geometric standards; attached to the probe to monitor stack gas velocity.

Draft Gauge - A dual-inclined oil gauge manometer made by Dwyer with a readability of 0.01-in. H_2O in the 0- to 1-in. range and 0.1-in. H_2O in the 1- to 10-in. range.

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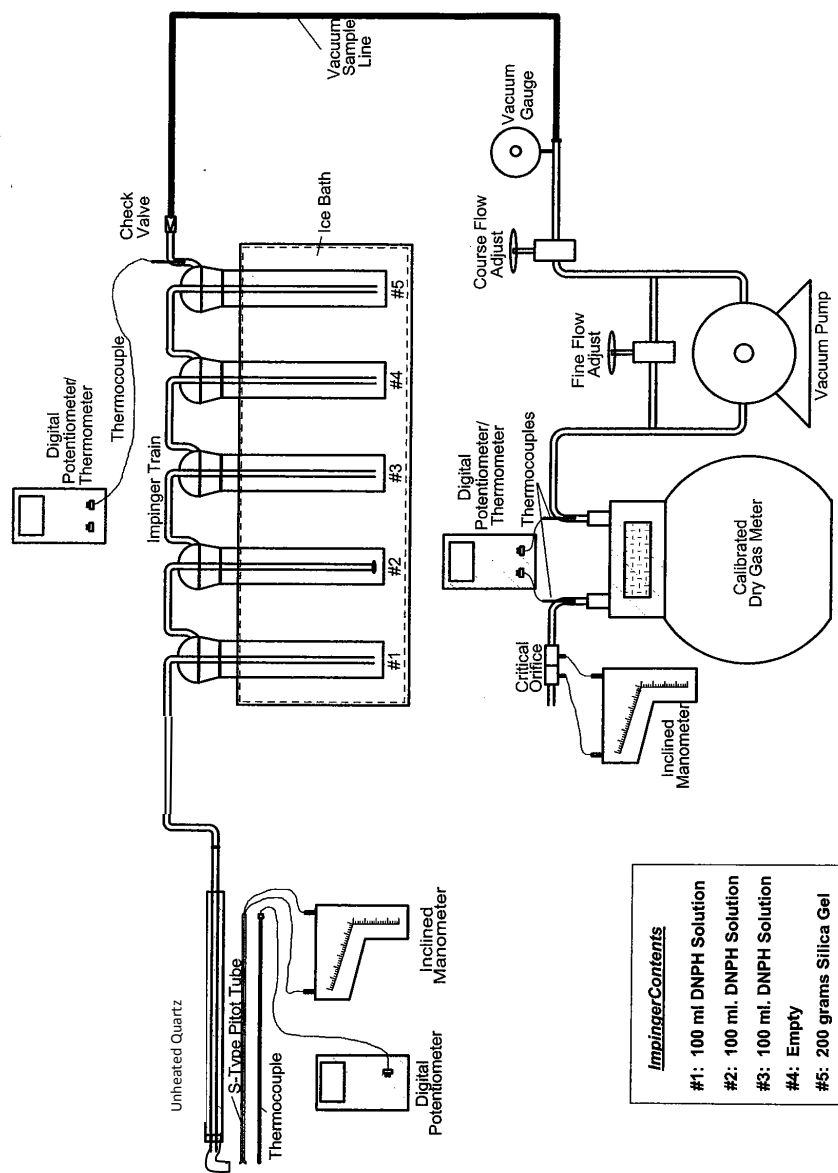


FIGURE 2-6. SW-846 METHOD 0011 SAMPLING TRAIN

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Impingers - Five impingers connected in series with O-ring ball joints. The first, third, fourth and fifth impingers are of the Greenburg-Smith design, modified by replacing the tip with a 1/2-in.-i.d. glass tube extending to 1/2-in. from the bottom of the flask. The first three impingers will contain a 2,4-dinitrophenylhydrazine (DNPH) solution.

Metering System - Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 5°F, dry gas meter with 2 percent accuracy, and related equipment to maintain an isokinetic sampling rate and to determine sample volume.

Barometer - Aneroid type to measure atmospheric pressure to ± 0.1 -in. Hg.

2.2.13.2 Sampling Procedures

Approximately 200 grams of silica gel will be weighed and placed in a sealed impinger prior to each test run. 200 mL of DNPH will be placed in the first impinger; the second and third impingers will each contain 100 mL DNPH; the fourth impinger will be empty, and the fifth impinger will contain silica gel. The sampling train will be leak-checked at the sampling site prior to each test run by plugging the inlet to the nozzle and pulling a 15-in. Hg vacuum; and at the conclusion of the test run, by plugging the inlet to the nozzle and pulling a vacuum equal to the highest vacuum reached during the test run.

The pitot tube and lines will be leak-checked at the test site prior to and at the conclusion of each test run. The check will be made by blowing into the impact opening of the pitot tube until 3 or more inches of water is recorded on the manometer and then capping the impact opening and holding it for 15 seconds to assure it is leak-free. The static pressure side of the pitot tube will be leak-checked by the same procedure, except suction is used to obtain the 3-in. H₂O manometer reading. Crushed ice will be placed around the impingers to keep the temperature of the gases leaving the last impinger at 68°F or less.

During sampling, stack gas and sampling train data will be recorded at each sampling point and whenever significant changes occur in stack flow conditions. Isokinetic sampling rates will be maintained within 10% of true isokinetic throughout the sampling period using isokinetic calculations. Sample rates will be less than 28 liters per minute.

2.2.13.3 Sample Recovery Procedures

The sampling train will be moved carefully from the test site to the cleanup area. The volume of DNPH from the first three impingers will be measured, and sample fractions will be recovered as follows:

Container 1 - Methylene chloride washings from all sample-exposed surfaces prior to the impinger train are placed in an amber glass container. Particulate is removed from the probe with the aid of a Teflon brush. The DNPH in the first three impinger sections of the sampling train is measured volumetrically and placed in the amber glass container. The impingers and connecting glassware are rinsed with methylene chloride and this rinse is added to the container for shipment to the laboratory. A final rinse of the impinger section is conducted using distilled H₂O and methylene chloride



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Container 2 - Sample blank equal in volume to the sample runs.

Container 3 - The silica gel from the fifth impinger is weighed, and this value is recorded on the Sample Recovery and Integrity Sheet along with other pertinent data. The color of the indicating silica gel will be observed to determine if there has been moisture breakthrough. The silica gel will be weighed to the nearest 0.5 g.

2.2.13.4 Analytical Procedures

The analytical procedures will follow those described in SW-846 Method 8315A.



SECTION THREE

Test Schedule

The proposed test schedule is presented in Table 3-1. The schedule below is based upon a crew of 7. Please note that this schedule is to be performed consecutively with the FCCU ICR test program to be conducted during the week of June 6, 2011. The schedule below may shift pursuant to completion of the FCCU ICR Test Program.

TABLE 3-1. PROPOSED TEST SCHEDULE

Day (2011)	Activity
1 (Monday 6/13)	Travel and set-up equipment. Valero electricians to connect 480-volt power upon ARI's arrival.
2 (Tuesday 6/14)	Conduct Group A1 for Volatile Organic HAP and Aldehydes (three 60-minute test periods).
3 (Wednesday 6/15)	Begin Group A2, A3 and F testing for Semi-Volatile Organic HAP (two 240-minute test periods); THC, CO, Methane and Ethane (two 60-minute test periods); and TRS, H ₂ S, COS and CS ₂ (two 180-minute test periods).
4 (Thursday 6/16)	Complete Group A2, A3 and F testing for Semi-Volatile Organic HAP (one 240-minute test period); THC, CO, Methane and Ethane (one 60-minute test period); and TRS, H ₂ S, COS and CS ₂ (one 180-minute test period); tear down equipment and remove from refinery.



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SECTION FOUR

Data Reduction and Report Format

Field test data will be recorded on ARI's standard field test data sheets.

Reduction of field test data will be accomplished through the use of computer programs to calculate gas parameter data and emission rates. All calculations including the equations used will be documented in the final report with all computer printouts included in the appendices. All field test data and test results are reviewed for completeness as well as accuracy prior to final reporting.

Following completion of field-testing, data reduction and analysis of collected samples, a comprehensive report of the test results will be prepared. The report format will be as follows:

- 1.0 INTRODUCTION AND SUMMARY OF TEST RESULTS
- 2.0 SAMPLING AND ANALYSIS PROCEDURES
- 3.0 PROCESS DESCRIPTION
- 4.0 TEST RESULTS AND DISCUSSION

APPENDICES

- A Calculation Summaries
- B Field Data
- C ARI Reference Method Monitoring Data
- D Analytical Data
- E Plant Operational Data
- F Test Equipment Calibration Data
- G Test Program Qualifications



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SECTION FIVE

Capabilities and Experience

ARI Environmental's offices in Wauconda, Illinois and Pasadena, Texas specialize in conducting stack emission, fugitive leak detection, ambient air and in-plant OSHA type testing for industrial clients.

ARI is organized so that its facilities and resources meet the requirements of ASTM D7036, Standard Practice for Competence of Air Emission Testing Bodies. ARI's laboratories in Pasadena, Texas and Wauconda, Illinois hold TCEQ NELAP Certificate No. T104704428-8A-TX. All test programs are supervised and conducted by onsite Qualified Individuals (QI) and/or Qualified Source Testing Individuals (QSTI) pursuant to ASTM D7036.

During the past 27 years, ARI personnel have conducted over 5,000 separate stack emission tests for a variety of industrial clients throughout North America for the determination of degree of source compliance and to yield emissions data and control equipment performance data for in-house engineering purposes.

ARI presently has over 80 trained personnel for conducting source emission sampling, fugitive leak detection monitoring, ambient air monitoring and OSHA sampling programs.

ARI has USEPA Method 5 particulate sampling trains, Method 17 particulate trains, TVA-1000 monitors and a variety of dataloggers for VOC leak detection programs, field use gas chromatographs and continuous FID units for hydrocarbon sampling, USEPA Method 18 and 25 sample trains, SO₂, NO_x and CO sampling and analysis equipment, Orsats for on-site gas composition analysis, and a modern, well equipped analytical laboratory for collected sample analyses including gas and liquid chromatography, GC/MS and FTIR capabilities.

ARI's eight mobile test trailers include full service Continuous Emissions Monitoring Systems for on-site analysis of CO₂, O₂, CO, NO_x, SO₂ and total hydrocarbons (THC). The data can be immediately accessed and reduced by ARI's data logger that is linked to a computer. This gives the client on-site knowledge of the testing program's results. The mobile test trailers also house an SRI Model 8610 Gas Chromatograph equipped with a Flame Ionization Detector (FID), a Thermal Conductivity Detector (TCD) and Flame Photometric Detector (FPD), GC/MS and FTIR for the on-site analysis of organics, inorganics and sulfur compounds.



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ATTACHMENT A

Method 18 Midget Impinger Method

