PALOS VERDES LANDFILL REMEDIAL INVESTIGATION REPORT

APPENDIX E.10

EMISSIONS TESTS; PALOS VERDES ENERGY RECOVERY FROM LANDFILL GAS (CARNOT)

EMISSIONS TESTS ON THE PALOS VERDES ENERGY RECOVERY FROM LANDFILL GAS (PVERG) FACILITY, UNIT 1, DECEMBER 1992

Prepared For:

COUNTY SANITATION DISTRICTS OF LOS ANGELES COUNTY Whittier, California

For Submittal To:

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

Prepared By:

Craig H. Fry

CARNOT Tustin, California

JANUARY 1993

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REVIEW AND CERTIFICATION

All work, calculations, and other activities and tasks performed and documented in this report were carried out under my direction and supervision.

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Craig H. Fry Assistant Manager Emission Measurement Division

Date $2/2/93$

I have reviewed, technically and editorially, details, calculations, results, conclusions and other appropriate written material contained herein, and hereby certify that the presented material is authentic and accurate.

Glunord Feldelfig Date 2-3-93

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Edward J. Filadelfia Senior Engineer

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SECTION 1.0

INTRODUCTION

Carnot was contracted by the County Sanitation Districts of Los Angeles County (LACSD) to perform a series of air emission related tests on the Palos Verdes Energy Recovery from Landfill Gas (PVERG) Facility, Unit 1. The tests were required by the South Coast Air Quality Management District (SCAQMD) to satisfy the requirements given in the SCAQMD Rule 1150.2, and the SCAQMD Permit to Construct Application No. 134321. Also, these tests were conducted to satisfy the California EPA (Cal-EPA) Toxic Substance Control requirements for the provisions on ambient air and landfill gas work plan for the Palos Verdes Landfill.

Emission tests were conducted on Unit 1 at the boiler exhaust and the landfill gas fuel supply (inlet). Table 1-1 presents a test matrix of the parameters measured at each location. The emission tests \cdot were conducted on December 30, 1992. Testing was performed by Craig Fry, Dave Evans and Robert Madrigal of Carnot. The testing was coordinated by Dr. Moon S. Chung of the LACSD. The boiler was maintained at steady load throughout the testing period by LACSD personnel.

A summary of the emission test results and the applicable permit limits for the parameters measured are presented in Table 1-2. Detailed test results are presented in Section 4.0. A discussion of the results and weather conditions occurring during testing are discussed in Section 5.0. All raw data and calculations can be found in the Appendices.

TABLE 1-1 TEST MATRIX

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TABLE 1-2 SUMMARY OF TEST RESULTS PVERG BOILER DECEMBER 30, 1992

NOTE: The results in this table are the averages of all measurements. See Section 4.0 for complete emission test results.

* - not measured.

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P/C - SCAQMD Permit Operating Condition Application No. 134321.

SECTION 2.0

TEST UNIT DESCRIPTION

The Palos Verdes Energy Recovery from Landfill Gas Facility (PVERG) consists of two identical Zurn Keystone landfill gas fired boilers. Unit 1 was tested in this emission test series. The steam production of both boilers is used to drive a steam turbine generator with a maximum electrical output of 13.0 megawatts. Each boiler fires approximately 3,600 scfm of landfill gas with supplemental natural gas which makes up 25% of the total Btu content. The natural gas is used because of the low Btu value (200 Btu/scf) of the inactive landfill gas fuel.

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SECTION 3.0

TEST DESCRIPTION

3.1 TEST CONDITIONS

LACSD personnel maintained steady load operations throughout the test period. The boiler was set to run at nominal load. Temperature, fuel flow rate and fuel Btu values were monitored by LACSD throughout the test periods. Table 3-1 summarizes the boiler operating conditions.

TABLE 3-1 PVERG TEST OPERATING CONDITIONS

3.2 SAMPLE LOCATIONS

Samples were collected from two locations in the landfill gas/boiler system. The locations were 1) the landfill fuel gas supplies and 2) the boiler exhausts. Access for sampling in the landfill gas fuel supply (inlet) was gained by removing a pipe plug downstream of the blower outlet and upstream of the boiler inlet. No isokinetic sampling was required at this location.

Samples from the boiler exhaust were collected via two ports in the stack wall. The ports are 4 inch I.D. and are located 90° apart on the circumference of the stack. The ports are 22 feet above the nearest flow disturbance and 5 feet, 5 inches below the stack top. Figure 3-1 is a schematic drawing of the PVERG stack sampling location. All tests requiring isokinetic sampling were conducted using 16

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point traverses of the sample plane.

3.3 TEST PROCEDURES

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The test procedures followed for the landfill gas and boiler exhaust measurements are summarized below in Tables 3-2 and 3-3, respectively. The selected procedures are consistent with those recommended by SCAQMD in their "Guidelines for Implementation of Rule 1150.1." Brief discussions of each procedure are given below in Sections 3.3.1 - 3.3.7.

TABLE 3-2 PVERG INLET TEST PROCEDURES

TABLE 3-3 PVERG EXHAUST TEST PROCEDURES

3.3.1 Methane and Total Gaseous Non-Methane Organics

Methane and total gaseous non-methane organics were measured using the draft SCAQMD Method 25.2. The inlet and exhaust samples were collected with Tedlar bags and analyzed by the TCA/FID. Atmosphere Assessment Associates performed the analyses on these samples within 72 hours after sampling. Inlet and exhaust were sampled simultaneously for a twenty-minute period.

3.3.2 Oxygen. Nitrogen. Carbon Monoxide. Carbon Dioxide and Nitrogen Oxides

Inlet O_2 , CO_2 and N_2 measurements were acquired from Tedlar bag samples and analyzed by GC/TCD using SCAQMD Method 10.1.

Measurements of NO_x, CO, O₂ and CO₂ at the exhaust were conducted using SCAQMD Method 100.1 sampling with a continuous emission monitoring system (CEM).

These CEM measurements were made using Carnot's continuous emissions monitoring system described in Appendix A. The system used a stainless steel probe connected to a 15' heater teflon line. Then the gaseous sample traveled through a moisture knockout cooled with ice and water. A peristaltic pump continuously drained the knock out. The sample then traveled to the ground via teflon line to an additional conditioning and filtering system.

Leak checks were conducted prior to and at the completion of the test project. The leak checks were conducted by operating the sample pump, plugging the probe inlet and all pressure side system exits except for one analyzer rotameter, then measuring the leakage rate on that rotameter.

EPA Protocol 1 Calibration Gas were used for CO and NO, analyzer calibration. All other gases were manufacturer certified to be $\pm 1\%$ and traceable to NIST. In accordance with SCAQMD Method 100.1 procedures, a pre- and post-test system bias check was conducted for each test run. The system bias check was conducted by delivering zero and span gas to the CEM probe tip and recording the asfound species concentration. No analyzer adjustments were made between these pre- and post-system bias checks. Calculations for the correction of measured system bias and instrument drift were then applied to each test run. The allowable limit of system bias deviation is *5%* of instrument range.

Duplicate emissions measurements were performed to determine nitrogen oxides and carbon monoxide emissions, as well as oxygen and carbon dioxide concentrations. The average concentrations were determined during each test for a period of 64 minutes. This test average was then corrected for measured system bias and drift. Exhaust N_z data was calculated by difference from the concentration of the other major exhaust gas components.

3.3.3 Moisture

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Moisture was measured in both the inlet and outlet streams of the boiler. SCAQMD Method 4.1 was used for the determinations.

Duplicate inlet measurements were made with a separate Method 4.1 train.

The moisture determinations of the flare exhaust were made in combination with the paniculate matter tests.

3.3.4 Flow Rate

Landfill gas flow rate into the boiler was set to specification using existing LACSD instrumentation on site, and was monitored and recorded throughout the test period. The inlet gas density is calculated using the concentrations of oxygen, carbon dioxide and methane. Outlet gas flow rate was determined in conjunction with all isokinetic tests using a combined pitot probe system.

3.3.5 Particulate Matter

Particulate matter concentration and emission rate were determined by wet impingement following SCAQMD Method 5.1. A quartz probe with a glass nozzle was used to sample the exhaust stream. Following the probe the sample travels through flexible teflon tubing to the impingers and then to a tared backup filter. A thermocouple and pitot probe are attached to the probe to facilitate isokinetic sampling at each of the 16 traverse points. Two ports were used to access the traverse points. Duplicate 64 minute samples were collected.

3.3.6 Trace Organic Hydrocarbons

Trace organic species were collected by Carnot in Tedlar bags and analyzed by GC/PID/ELCD by the LACSD lab at JWPCP using the EPA Method T03 and analyzed within 72 hours of sampling. Inlet and exhaust were sampled simultaneously for a twenty-minute period. The flow rate used to calculate the lb/hr emission rates are from the paniculate matter test flow rate being performed concurrently with trace organic sampling.

3.3.7 Hydrogen Sulfide and Reduced Sulfur Compounds

Samples for determination of hydrogen sulfide and reduced sulfur compounds were collected in Tedlar bags. The samples were analyzed by GC/FPD/ELCD by the LACSD lab at JWPCP and analyzed within 8 hours of sampling.

SECTION 4.0

RESULTS

The results of the test are presented in the following tables:

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TABLE 4-1 GENERAL RESULTS PVERG, UNIT 1 DECEMBER 30, 1992

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TABLE 4-2 TRACE ORGANIC SPECIES DESTRUCTION EFFICIENCY RESULTS PVERG UNIT 1, TEST NO. 1 DECEMBER 30, 1992

Row rate, Inlet dscfm How rate, Exhaust dscfm Species Methylene Chloride: lb/hr Chloroform: lb/hr 1,1,1 -trichloroethane: lb/hr Carbon Tetrachloride: lb/hr 1,1-dichloroethene: lb/hr Trichloroethylene: . lb/hr Tetrachloroethylene: lb/hr Chlorobenzene: lb/hr Vinyl Chloride: lb/hr m-dichlorobenzene: 1 lb/hr o + p dichlorobenzene: lb/hr 1.1 -dichloroethane: lb/hr 1,2-dichloroethane: lb/hr Benzene: lb/hr Toluene: lb/hr Acetonitrile: lb/hr m-xvlenes: lb/hr o+p xylenes: lb/hr 1,2-dibromoethane: lb/hr Benzyl Chloride: lb/hr 3589 14576 Inlet 200 ppb 9.64 x 10-' $ND < 200$ ppb
 $< 1.35 \times 10^{-2}$ $ND < 200$ ppb $< 1.51 \times 10^{22}$ $ND < 200$ ppb
 $< 1.75 \times 10^{-2}$ ND < 200 ppb < 1.10 x 10'² 500 ppb 3.73×10^{-2} 400 ppb 3.76×10^{-2} 4700 ppb 3.00×10^{-1} 1400 ppb 4.97 x 10-² ND < 200 ppb $<$ 1.67 x 10⁻² 1300 ppb 1.08 x 10-' $ND < 200$ ppb
 $< 1.12 \times 10^{-2}$ ND < 200 ppb $<$ 1.12 x 10⁻² 11000 ppb 4.88×10^{-1} 24000 ppb 1.25 x 10° ND < 2000 ppb $<$ 4.66 x 10² 25000 ppb 1.51 x 10° 21000 ppb 1.27 x 10° ND < 7000 ppb $< 7.46 \times 10^{-7}$ $ND < 5000$ ppb
 $< 3.59 \times 10^{-1}$ Exhaust ND < 0.2 ppb

<3.91 x 10⁻⁵ $ND < 0.2$ ppb
 $< 5.50 \times 10^{-5}$ $ND < 0.2$ ppb
 $< 6.15 \times 10^{-5}$ $ND < 0.2$ ppb
 $< 7.09 \times 10^{-5}$ ND < 0.2 ppb

<4.47 x 10^{.5} $ND < 0.2$ ppb
 $< 6.06 \times 10^{-5}$ ND < 0.2 ppb

<7.64 x 10⁻⁵ $ND < 0.4$ ppb $< 1.04 \times 10^{-4}$ ND < 0.4 ppb < 5.76 x 10'⁵ $ND < 0.2$ ppb $< 6.78 \times 10^{-5}$ $ND < 0.2$ ppb
 $< 6.78 \times 10^{-5}$ $ND < 0.2$ ppb
 $< 4.56 \times 10^{-5}$ $ND < 0.2$ ppb $<$ 4.56 x 10⁻⁵ 0.2 ppb
3.60 x 10^{.5} $ND < 1$ ppb $< 2.12 \times 10^{-4}$ ND x 2 ppb $< 1.89 \times 10^{-4}$ $ND < 0.2$ ppb
 $< 4.89 \times 10^{-5}$ ND < 0.2 ppb

< 4.89 x 10⁻⁵ ND < 7 ppb < 3.03 x 10"^J $ND < 5$ ppb $<$ 1.46 x 10³ Destruction Efficiency, % > 99.59 NA NA NA NA > 99.84 > 99.80 > 99.97 > 99.88 NA > 99.94 NA NA 99.99 > 99.98 NA 100.00 100.0 NA NA

ND < indicates that the species was not detected. Values indicate the detection limit for this species and the concentration is less than the presented value. NA - indicates that the destruction efficiency cannot be calculated because the concentration is below detection limits.

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TABLE 4-3 TRACE ORGANIC SPECIES DESTRUCTION EFFICIENCY RESULTS PVERG UNIT 1, TEST NO. 2 DECEMBER 30, 1992

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ND< indicates that the species was not detected. Values indicate the detection limit for this species and the concentration is less than the presented value.
NA - indicates that the destruction efficiency cannot be calcula

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APPENDIX A MEASUREMENT PROCEDURES

Continuous Emissions Monitoring System Oxygen *(O₂)* by Continuous Analyzer Carbon Dioxide (CO₂) by Continuous Analyzer NO/NO, by Continuous Analyzer Carbon Monoxide (CO) by NDIR/Gas Filter Correlation Total Particulate by SCAQMD Wet Impingement Method Hydrocarbons by SCAQMD Micro TCA Method Stack Gas Velocity and Volumetric Flow Rate Determination of Moisture in Stack Gases Procedure 280A: Gas Chromatographic Analysis of Volatile Sulfur Compounds Procedure 600B: Gas Chromatographic Analysis of Organic Compounds in Air and Gas Samples Using a Packed Column Procedure 600C: Gas Chromatographic Analysis of Acetonitrile in Air and Gas Samples Using a Packed Column Procedure 1203A: Gas Chromatographic Analysis of Air, Methane and Carbon Dioxide Using a Packed Column

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Continuous Emissions Monitoring System

 O_2 , CO, CO₂, NO, NO₂ and SO₂ are measured using an extractive continuous emissions monitoring (CEM) package, shown in the following figure. This package is comprised of three basic subsystems. They are: (1) the sample acquisition and conditioning system, (2) the calibration gas system, and (3) the analyzers themselves. This section presents a description of the sampling and calibration systems. Descriptions of the analyzers used in this program and the corresponding reference test methods follow. Information regarding quality assurance information on the system, including calibration routines and system performance data follows.

The sample acquisition and conditioning system contains components to extract a representative sample from the stack or flue, transport the sample to the analyzers, and remove moisture and particulate material from the sample. In addition to performing the tasks above, the system must preserve the measured species and deliver the sample for analysis intact. The sample acquisition system extracts the sample through a stainless steel probe. The probe is insulated or heated as necessary to avoid condensation. If the paniculate loading in the stack is high, a sintered stainless steel filter is used on the end of the probe.

Where water soluble $NO₂$ and/or $SO₂$ are to be measured, the sample is drawn from the probe through a heated teflon sample line into an on-stack cooled (approximately 35-40°F) water removal trap. The trap consists of stainless steel flasks in a bath of ice and water. This design removes the water vapor by condensation. The contact between the sample and liquid water is minimized and the soluble $NO₂$ and $SO₂$ are conserved. This system meets the requirements of EPA Method 20. The sample is then drawn through a teflon transport line, paniculate filter, secondary water removal and into the sample pump. The pump is a dual head, diaphragm pump. All sample-wetted components of the pump are stainless steel or teflon. The pressurized sample leaving the pump flows through a third condensate trap in a refrigerated water bath ($\approx 38^{\circ}$ F) for final moisture removal. A drain line and valve are provided to constantly expel any condensed moisture from the dryer at this point. After the dryer, the sample is directed into a distribution manifold. Excess sample is vented through a back-pressure regulator, maintaining a constant pressure of 5-6 psig to the analyzer rotameters.

The calibration system is comprised of two parts: the analyzer calibration, and the system bias check (dynamic calibration). The analyzer calibration equipment includes pressurized cylinders of certified span gas. The gases used are, as a minimum, certified to 1 *%* by the manufacturer. Where necessary to comply with reference method requirements EPA Protocol 1 gases are used. The cylinders are equipped with pressure regulators which supply the calibration gas to the analyzers at the same pressure and flow rate as the sample. The selection of zero, span, or sample gas directed to each analyzer is accomplished by operation of the sample/calibration selector fittings.

The system bias check is accomplished by transporting the same gases used to zero and span the analyzers to the sample system as close as practical to the probe inlet. This is done either by attaching the calibration gas supply line to the probe top with flexible tubing or by actuation of a solenoid valve located at the sample conditioner inlet (probe exit). The span gas is exposed to the same elements as the sample and the system response is documented. The analyzer indications for the system calibration check must agree within 5% of the analyzer calibration. Values are adjusted and changes/repairs are made to the system to compensate for any difference in analyzer readings. Specific information on the analytical equipment and test methods used is provided in the following pages.

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Method:

Reference:

Principle:

Sampling Procedure:

Total Particulate by SCAQMD Wet Impingement Method

SCAQMD Method 5.1

A metered flue gas sample is withdrawn isokinetically and particulates are collected in a series of water impingers followed by a backup filter.

The sample train used in the tests is shown in the following figure. The sample is drawn isokinetically through a stainless steel or glass nozzle and probe. The probe is connected to an impinger train by Teflon tubing. The train consists of two Greenburg-Smith impingers which contain 100 ml of distilled water, an empty impinger as a knockout, a 100 mm glass fiber filter, and an impinger containing silica-gel to protect the leak-tight vacuum pump and calibrated dry gas meter from moisture. The impingers are designed to collect particles larger than one micron, and will also collect some smaller water-soluble particles. The backup filter collects any particulate that is not collected in the impingers. Th is material collected in the backup filter consists of submicron-sized droplets of condensed organic vapors.

Sample Train for Determination of Total Particulate by SCAQMD Wet Impingement Method

SCAQMD Method 4.1 (moisture) and Methods 1.1 and 2.1 (velocity) are performed in conjunction with the test. Stack velocity is measured during the test to maintain isokinetic sampling and to measure stack flow rate. Moisture concentration is determined by weighing the impingers before and after sampling to determine the amount of moisture collected.

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Sample Recovery and Analysis:

Following testing, the probe, sample line, and impingers are washed with water. The entire rinse and sample is then filtered through a tared filter to recover large particles. An aliquot of the rinse is evaporated in a tared glass beaker at 105°C, and the residue is determined gravimetrically. If the sample contains semi-volatile hydrocarbon species that might be lost by evaporating at 105° C, the sample is extracted with methylene chloride to remove those species, and the methylene chloride fraction is evaporated at ambient temperature and weighed.

The backup filter is baked at 105°C, desiccated, cooled, and weighed, and the weight combined with the boildown and other filter to determine the total particulate catch.

If there are high concentrations of $SO₂$ in the gas stream, a positive interference can be caused by oxidation of SO_2 to sulfuric acid in the impingers. In this case, the boildown residue is analyzed for sulfuric acid (either by titration or precipitation) and the acid is subtracted from the particulate catch as $H_2SO_42H_2O$. Since this fraction includes both SO,-related "pseudo-particulate" as well as the true particulate species SO_3 , a separate test for SO_3 is run and the measured SO_3 is added back to the particulate catch as $H_2SO_4 2H_2O$.

Method:

Hydrocarbons by SC AQMD Micro Total Carbon Analysis (TCAyFID) Method

Reference:

Principle:

A Tedlar bag is filled with flue gas at a constant rate. The bag contents are analyzed by gas chromatography/flame ionization detection for CO, $CO₂$, methane and total gaseous non-methane hydrocarbons.

Sampling Procedure: Samples are collected using a lung-type sampling system shown in the attached figure. In this system, a bag is placed in a sealed container and the container is evacuated. Flue gas enters the bag as it expands to fill the container. Sampling rate is monitored by a rotameter on the container exhaust. This system allows sample collection without exposing the sample to pumps, flowmeters, oils, etc.

SCAQMD Method 25.2 (draft Source Test Manual)

Sample Train for Determination of Hydrocarbons by SCAQMD Micro TCA Method

Analytical Procedure:

In the analytical phase, gaseous carbon compounds from the tank are fractioned on a chromatographic column, eluting in the order: carbon monoxide, methane, carbon dioxide, non-methane hydrocarbons. All resulting vapors are passed through oxidizers where they are combusted to carbon dioxide, then converted to methane and measured by flame ionization detection. $CO₂$, $CO₂$, $CH₄$, and total gaseous non-methane hydrocarbons are reported separately.

This method provides lower detection limits than the standard TCA procedure, which uses GC/NDIR. Since this method does not use a steel condensate trap, it eliminates positive interferences that have been associated with carbon dioxide dissolved in water frozen in the condensate trap and released during analysis.

The TCA/FID method is appropriate for combustion sources and ambient sampling where low concentrations of hydrocarbons are expected.

Carnot subcontracts TCA analysis to qualified local laboratories experienced in the analytical procedures.

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Method: **Stack Gas Velocity and Volumetric Flow Rate**

Reference: EPA Method 2, SCAQMD Method 2.1, ARB Method 2

Principle: The average gas velocity in a stack is determined from the measurement of the gas density and from the measurement of the average velocity head using a Type-S (Stausscheibe) Pitot tube.

Sampling The velocity head and temperature are measured at traverse points specified by EPA Method Procedure: 1 or SCAQMD Method 1.1. The velocity is measured using a Type-S Pitot tube and an inclined water manometer. The flow coefficient of the pitot tube is known. Temperature of the gas is measured using a thermocouple. The stack gas molecular weight is determined from independent measurements of O_2 , CO_2 , and H_2O concentrations.

Sample The stack gas velocity is determined from the measured average velocity head, the measured Analysis average temperature, the measured average duct static pressure, the measured dry and Recovery: concentrations of O_2 and CO_2 , and the measured concentration of H_2O . The velocity is determined from the following set of equations:

$$
MW_{\text{wet}} = \left[(0.44)(\%CO_2) + (0.32)(\%O_2) + (0.28)(\%N_2) \right] (1 - \frac{\%H_2O}{100}) + (18)(\frac{\%H_2O}{100})
$$

The stack gas volumetric flow rate is determined from the measured stack gas velocity, the area of the stack at the measurement plane, and the measured gas temperature and pressure. The volumetric flow rate is determined from the following set of equations:

$$
Q = (V_s)(AREA)(60)
$$
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\n
$$
Q_{ws} = Q \left[\frac{T_{ref}}{T_s} \right] \left[\frac{P_s}{29.92} \right]
$$
 [wscfm]
\n
$$
Q_{sd} = Q_{ws} \left[1 - \frac{\%H_2O}{100} \right]
$$
 [dscfm]

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Method:

Applicable Ref. Methods:

Principle:

EPA 4, ARB 1-4, SCAQMD 4.1

Determination of Moisture in Stack Gases

A gas sample is extracted at a constant rate from the source; moisture is removed from the sample stream and determined volumetrically or gravimetrically.

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Sampling Procedure: The sample train used in the tests is shown in the following figure. The sample is drawn at a constant rate through a stainless steel probe. The probe is connected to an impinger train by Teflon tubing. The train consists of two Greenburg-Smith impingers which contain 100 ml water, an empty impinger as a knockout, and an impinger containing silica gel to protect the pump from moisture.

Sample Train for Determination of Moisture by EPA Method 4

Sample Recovery and Analysis:

Following testing, moisture content is determined gravimetrically from initial and final impinger weights.

2S0A. GAS CHROMATOGRAPHIC ANALYSIS OF VOLATILE SULFUR COMPOUNDS

INTRODUCTION

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Gaseous sulfur compounds are cryogenically collected on a solid phase sorbent trap and analyzed by packed column gas chromatography. The gas chromatograph is equipped with two different columns and two different detectors operating in parallel in order to effect positive identification and quantitation of the target analytes.

Procedure 280A: Gas Chromatographic Analysis of Volatile Sulfur Compounds (12-31-91)

- 1. Scope and Application
	- 1.1 This procedure is used for the identification and quantitation of the sulfur gases listed in Table I. Quantitation may be carried out at the ppb level under proper conditions.
	- 1.2 Samples encountered include landfill, digester and sewer gas and ambient air. This analytical method requires a 30 minute chromatographic run and is used for ppb-level analysis of a wide range of sulfur compounds. An abbreviated method which measures the target compound list of SCAQMD Rule 1150.1 at the part-per-million level requires a 15 minute run.
- 2. Summary of Procedure
	- 2.1 Known amounts of sample gas are passed through liquid nitrogen-cooled traps. The traps are swept with helium to remove oxygen and nitrogen and are then heated to desorb the trapped sulfur gases onto cooled $(-60^{\circ}C)$ gas chromatographic columns. The columns are then heated at a rate which allows these compounds to be separated on the respective columns. The two detectors, a flame photometric detector (FPD) and a Hall electrolytic conductivity detector (HECD), may be interchanged if further confirmatory analyses are necessary.
- 3. Sample Handling and Preservation
	- 3.1 Samples are normally collected in Tedlar (polyvinyl fluoride) bags and brought to the laboratory for analysis. Samples should be stored in the dark and away from heat. Samples should be analyzed within twenty-four hours. This is especially important when high concentrations (1 ppm) of methyl mercaptan are suspected.

4. Interferences

4.1 The flame photometric detector operates by detecting the fluorescence of S, molecules formed from sulfur atoms which are liberated when sulfur-containing species are burned in a hydrogen/air flame. Since the fluorescence intensity is directly proportional to the concentration of S_2 molecules and to the square of the sulfur-atom concentration in the flame, the detector signal will be roughly proportional to the square of the amount of sulfur-containing species reaching the detector. For this to be true, equilibrium must be rapidly established in the flame between sulfur atoms and S, molecules. This will occur if the concentration of sulfur-containing species is small compared to the concentration of hydrogen and oxygen. If the detector is overloaded, a chemical saturation of the detector will occur and there will be a loss of sensitivity. This chemical saturation will normally occur at a higher concentration than is required to saturate the photomultiplier and so should not be a problem.

- 4.2 The FPD has a very large rejection ratio for non-sulfur-containing species, so there are very few interferences.
- 4.3 Ethyl mercaptan and dimethyl sulfide co-elute on the Chromosil 330 column under the conditions used in this procedure, but they are completely separated on the XE-60 column.
- 4.4 The sulfur mode HECD reacts sulfur-containing compounds with an excess of oxygen to form SO,/SO,, which is then detected in the conductivity cell. The response due to any CO, formed under these oxidizing conditions is levelled by employing a non-aqueous solvent (reagent methanol) to prevent the formation of carbonic acid. Since hydrogen halides will also be formed even under oxidizing conditions, the sulfur mode HECD employs a copper tube containing a silver wire between the reactor and detector as a hydrogen halide scrubber to eliminate interferences from halogenated compounds. This scrubber is not so effective in removing hydrogen fluoride as it is in removing the other halides, and so interferences due to fluorinated hydrocarbons can occur, especially in the region where the C3 and C4-mercaptans elute. Sewer gas typically shows several large peaks in this region which are not due to sulfur containing compounds.
- 4.5 Since the Chromosil 330 column has an upper temperature limit of 100°C, the XE-60 column cannot be used close to its upper temperature limit. Under these conditions, the retention times of the C3- and higher mercaptans on the XE-60 may be unacceptably long, and the usefulness of the XE-60 is limited to the quantitation of the Cl- and C2-mercaptans and sulfides of the SCAQMD rule 1150.1 list.

5. Apparatus

- 5.1 Varian Model 3400 gas chromatograph equipped with a Varian dual-flame FPD and a Tracor Model 700A HECD operated in the sulfur mode.
	- 5.1.1 Columns:
		- a. 8'(6' packed) x 1/S"OD Teflon (FEP) packed with Chromosil 330.

b. 6' x 1/4"OD (2 mm id) glass packed with 1.5% XE-60/1.0% H_iPO₄ on Carbopak B. (The glass column must be deactivated before packing by baking at 130°C for six hours with a carrier gas flow rate of 100-200 mL/min.)

5.1.2 Operating Parameters

Carrier gas: Helium (carrier grade), 25 mL/min (column a), 30 mL/min (column b). Detector temperature: 180°C FPD Range: 10exp(-8) PMT voltage: 480-520 volts HECD Range: 100 HECD Solvent: 100% methanol (reagent grade)

Temperature program: 3.5 minute hold at initial temperature of -60°C. Program to 40°C at 40° C/minute and hold for 4.5 minutes. Program to 65° C at 40°C per minute and hold for 3.0 minutes. Program to 95°C at 40°C/min and hold for 15 minutes. Vent closes at 4.5 min. and opens at 14.75 min.

- 5.2 Data System: Nelson Analytical (3000 Series) chromatography software installed on an IBM PS/2 with a two-channel buffer box (760 Series) to collect raw data from both detectors simultaneously.
- 5.3 Cryo-adsorbent Trapping System
	- 5.3.1 Plumbing: 1/8" or 1.16" Teflon tubing used throughout.
- 5.3.2 Trap design: Two similar U-shaped traps are constructed of 1/8" OD Teflon-lined stainless steel (1.8 mm ID) and packed with 0.1 gram 50/SO mesh Porapak QS. The jacket consists of 1/4" OD copper tubing with Swagelock TEE fittings at the ends. The jacket is wrapped with $12'$ x $3/16''$ nichrome heating cord controlled by a Cole-Parmer model 2149-00 temperature control relay. The trap is heated to approximately 210°C during the desorption cycle. The trap is cooled by flowing liquid nitrogen through its outer jacket.
- 5.4 Sample Loading:

a) small volume samples (1-50 mL) are injected by gas-tight syringe directly into the sweep helium and are deposited on the trap.

b) large volume samples are withdrawn from sample bags with 100 mL glass syringe with Teflon plunger and forced through trap.

- 5.5 Sample Injection: Samples are transferred from the two traps and injected onto the two columns using twin Valco E60 two-position electric actuator/valve assemblies. Valves are actuated by relays controlled by the GC method which injects at 0.5 min and returns to load position at 10 min. Valves are fabricated from Hastelloy C in order to minimize sulfur gas adsorption and reactivity.
	- 5.5.1 Pneumatics and valves. Samples are introduced through the syringe or through a septum port. The sample gas flows though the trap switch valve into the proper injection valve and liquid nitrogen-cooled trap. With the trap

switch valve in the LOAD A position, the sample is directed to injection valve A and the sweep helium flows through injection valve B. When this valve is in the LOAD B position, sample gas flows to valve B and sweep helium to valve A. Sweep helium can be directed to both injection valves and traps simultaneously by removing the sample needle from the sample bag and inserting it in the sweep helium septum port.

When the sample gas reaches the proper injection valve, it is directed to the liquid nitrogen-cooled trap where the less-volatile species are adsorbed on the Porapak QS. The sweep helium then removes most oxygen, nitrogen and other permanent gases and sends them out the vent. When the valve is turned to the INJECT position, the carrier helium flow is directed to backflush the trap onto the gas chromatographic column and the sweep helium is vented. The two injection valves are configured identically.

After the separated analytes exit the chromatographic columns, they are directed to the detector switch valve. This is a four-port Hastelloy C valve which allows column effluent to be directed to either of the two detectors. Normal configuration has Chromosil 330 effluent going to the flame photometric detector and XE-60 effluent to the HECD.

5.6 Electrical connections. Electrical connections are made between the Varian 3400, the Nelson 760 buffer box, the IBM PS/2, and the cryo-adsorbent system.

The 760 interface is the heart of the system, as it provides the interface between the other members. The connections to the 760 are shown. J101 is the connection to the IBM PC/AT. Jl is the 14-pin connector carrying the relays which control the injection valves, the liquid nitrogen flow to the traps and the trap heaters. Only relays 2 through 7 are used: relays 1 and 8 are reserved by Nelson for use with autosamplers. DET A $+/-$ and DET B $+/-$ are the inputs from the FPD and HECD, respectively. The FPD signal is taken from the side port on the Varian 3400 and HECD signal is taken from the 10VFS and COMP COM terminals on the back of the Tracor 700A module. The START NO IN/COM terminals are connected to J23 in the Varian 3400. This terminal provides a one-second contact closure when the START button in the *GC* is pushed and is used to provide a "start" signal to the Nelson system. Unused terminals on the Nelson 760 box include the J2 BCD connector and the READY IN/COM connections.

Relay 2 activates the liquid nitrogen flow to the traps and can be manually deactivated at the toggle switch mounted below the traps. Relay 3 controls the trap heaters and can also be manually deactivated by a Cole-Parmer 2149 temperature control relay. Relays 4 and 5 control the position of injection valve A. Relay 4 is activated to move the valve to the INJECT position and relay 5 is activated to return the valve to the LOAD position. Relays 6 and 7 serve the analogous functions on injection valve B. The relays are normally controlled by the Nelson software.

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Output from the detectors is also directed to a strip chart recorder in order to provide real-time monitoring of the chromatographic runs.

5.7 Safety Precautions

Liquid nitrogen is used as a coolant for both the adsorbent traps and the column oven. Caution must be exercised due to the possibility of freeze burns caused by exposure of skin to extremely low temperatures. Avoid contact with any metal tubine through which liquid nitrogen is flowing and make sure that the exhaust vents *on* the adsorbent traps are pointing away from anyone in the laboratory.

Gaseous nitrogen is also an asphyxiant. Since the adsorbent traps use large quantities of liquid nitrogen during each run, the possibility exists that room oxygen could be depleted if the ventilation system fails. Do not operate the system if the laboratory ventilation system is not functioning properly.

When liquified gases vaporize, they expand to approximately 700 times their liquid volumes. Thus, the very real possibility exists for a violent rupture of the liquid nitrogen line if liquid nitrogen is confined between two valves with no access to a relief valve. Make absolutely sure that there is a relief valve between any two closures or valves. ANY SECTION OF ISOLATED LINE MUST BE VENTED OR HAVE A PRESSURE RELIEF VALVE!

6. Standards

6.1 Hydrogen sulfide, carbonyl sulfide, methyl mercaptan. ethyl mercaptan, carbon disulfide and dimethyl sulfide are obtained from Scott Specialty Gas cylinders in 100 ppm v/v (nominal) concentrations. A second cylinder containing approximately 5 ppm v/v H.S and 2 ppm v/v each of the other above-named species except ethyl mercaptan is used for daily calibrations. Sulfur dioxide, ethyl mercaptan, and DMDS are taken from separate cylinders containing 5 ppm v/v SO₂, 2 ppm ethyl mercaptan, and 4.6 ppm v/v DMDS in nitrogen.

A stock solution of 0.5% v/v (in methanol) of the heavier components (C3 and higher mercaptans and sulfides) is used to make up the rest of the standards, if needed. The stock solution is prepared by using a 0.05 mL syringe to place 0.05 mL of each of the neat compounds in a 10 mL volumetric flask partially filled with methanol and then diluting to 10 mL. These compounds are obtained from Aldrich (typically 98-99% purity) and are used with no further purification.

6.2 Preparation of standards. The Scott 5 ppm/2 ppm v/v standards are taken directly from the cylinder with no further preparation. Two ppm bag standards are made from 100 ppm v/v Scott cylinders by injecting 40 mL of the gas into a Tedlar bag filled with 1960 mL of nitrogen. Bag standards of the heavier components are made by injecting 1 microliter of the 0.5% liquid standard into a Tedlar bag filled with 1 liter of nitrogen. This will give the following concentrations: C3 mercaptans. 1.3 ppm; C4 mercaptans. 1.1 ppm; dimethyl disulfide. 1.4 ppm; and thiophene (if used), 2.2 ppm.

7. Procedure

7.1 Load method CROM33AD into the Nelson box.
7.9 Calibration curves. Six-point calibration data are generated by injecting 0.5, 1, 2, 5, 10 or 15 mL of the Scott 5 ppm/2 ppm v/v standard on the FPD side, and 0.2, 1, 2, 5, 10, or 15 ml on the HECD side. The C3-C4 mercaptan standard is injected on the Chromosil 330 side only, due to the unacceptably long retention times of these compounds on the XE-60 column. Since dimethyl sulfide and ethyl mercaptan coelute on the Chromosil 330 column, ethyl mercaptan is injected only on the XE-60 column. The areas and retention times are stored under MMDDFW for FPD (W=volume injected) and MMDDHW for HECD.

Calibration curves are generated by entering peak area counts versus component concentration in the appropriate recalculation method. Calibration data are generated by using a varying injection volume of constant concentration instead of a constant volume of varying concentration, so a universal unit of ppm-mL is used in the recalculation methods instead of a concentration. Differences in injection volume are accounted for in the recalculation methods. The 15 mL injection of hydrogen sulfide is not used on the FPD calibration due to poor fit on the curve.

- 7.10 Updating calibration curves. Calibration curves are updated by averaging the current peak areas with the existing peak areas. This procedure weights the updated calibration point heavily in favor of the current day's response, but does not ignore the past history of the instrument response. The new calibration points should agree to within $+/-20\%$ of the current point since these should not be taken until after "normal" response has been verified. If there is a gross discrepancy, a faulty injection should be suspected.
- 7.11 Recalculation methods. The Nelson method CROM33AD is used to control the relays and data acquisition. Data are stored in files named CHROMxxx (FPD data) and DHROMxxx (HECD data). Recalculation methods for these data are MMFPDDD and MMSHALDD. respectively, which contain the calibration curves for each column/detector combination.
- 7.12 The calibration curves cover a concentration range of greater than one order of magnitude. There are many samples which will generate analyte peaks which are either above or below the range of peak areas covered by the curves. In these cases it may be necessary to perform a second analysis using a larger or smaller injection volume, as appropriate.
- 7.13 Each chromatographic run must be reviewed soon after its completion in order to detect any range, interference or instrumental problems which would require a repeat analysis. Next-day review is not acceptable due to the possibility of sample degradation. Although the stability limits of the target compounds have been established when they are at low concentration in pure air or nitrogen, the complex nature of the samples usually received precludes the assumption of their long-term stability.

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8. Calculations

8.1 The flame photometric detector response is inherently nonlinear, and calibration data

are fitted to a quadratic function of the form

 $A = a(X)^{2} + b(X) + c$

where A is the peak area. (X) is the analyte concentration in ppm-mL units, and a, b, and c are coefficients generated by the Nelson curve-fitting algorithm. To find the actual sample concentration, Nelson solves for X and divides this value by the injection volume:

Concentration = $(X)/V$

where V is the injection volume.

The Nelson software should find the analyte concentration by solving the quadratic equation when given the analyte peak area and injection volume. However, several versions of the Nelson software are known to contain bugs which prevent the quadratic from being solved correctly. It is then necessary to manually perform the required calculations.

- 8.2 The Hall detector calibration data is plotted on a point to point curve. At higher concentrations, the hydrogen sulfide data is better fitted on a cubic fit equation.
- 8.3 Detection limits have been established for the Chromosil 330/FPD and XE-60/HECD combinations according to the EPA approved method of Glaser, et.al. Most of the target analytes containing one sulfur atom have a detection limit of about 2.5 ppb (assuming a 500 mL injection) on the Chromosil 330/FPD. Compounds such as carbon disulfide and dimethyl disulfide which have two sulfur atoms have somewhat lower limits. Detection limits on the XE-60/HECD have not been completely determined; however it is known that they are well below one part-per-billion (again assuming a 500 mL injection) for all target analytes. If a 5 mL injection volume is used the reporting limits will be ≤ 0.1 ppm for the aforementioned areas. Any components that are below the lowest calibration point are reported as less than whatever that calibration point is. Because the XE-60/HECD combination is more sensitive and it separates all 1150.1 compounds, the reported detection limits for the 1150.1 compounds are usually based on this detector/column combination.
- 8.4 Equations used in standards preparation. Concentrations of Tedlar bag standards prepared from Scott cylinders may be calculated from the equation

 $C(bag) = C(Scott) \times V(s)/V(tot)$

Where C(bag) is the concentration of the standard, C(Scott) is the concentration of the relevant component in the Scott cylinder, $V(s)$ is the volume of the standard injected into the bag, and $V(101)$ is the total volume of standard and diluent in the bag.

Concentrations of standards prepared from the 0.5% liquid standards may be calculated from the equation

$$
C(bag) = \frac{V \times d \times 10 \times 22.4 \text{ L/mole} \times C(comp)}{Mw \times V(bag)}
$$

where V is the volume of liquid standard in microliters injected into the Tedlar bag, d is the density of the relevant component in g/mL , C (comp) is the concentration of a given component of the liquid standard in volume percent, 22.4 L/mole is the molar volume of a gas at room temperature, Mw is the molecular weight of the component in amu, and $V(bag)$ is the volume of diluent gas in liters. If $C(comp)$ is assumed to be 0.5%, this equation reduces to

$$
C(bag) = \frac{V \times d \times 112}{Mw \times V(bag)}
$$

Note that if a new liquid standard is prepared with a component concentration other than 0.5%, the constant term in this equation will have to be multiplied by a factor of

$$
x/0.5 \quad (=2x)
$$

where x is the per cent concentration of a given component in the new standard.

- 9. Quality Assurance Guidelines
	- 9.1 A duplicate and spike will be run every tenth sample.
	- 9.2 AUTOSQC. The area tables should be entered under FPDSGC and HECDSGC. The retention times are entered under FPD-RT and HECDS-RT. For each detector, a "warning situation" exists whenever any component is out by two standard deviations. A "out of control" situation exists whenever any component is out by 3 standard deviations. Since two detectors are used, you may still be able be able to do the analysis using the other detector, if it is in control.

If a "warning" or "out of control" situation occurs, then re-inject the standard. If a "out of control" situation repeats, then investigate for possible causes of the problem. If the problem cannot be resolved, then the detector response must be re-calibrated. If a "warning" situation repeats, then investigate for possible causes of the problem. If the problem cannot be resolved, then the samples may still be run. If a "warning" situation persists for three days, then it is considered "out of control".

After the problem has been resolved, then delete all "out of control" points from the control charts. Do not remove the "warning" points.

- 9.3 Spikes for qualitative analysis.
	- 9.3.1 Spikes are employed to confirm the identity of the higher molecular weight analytes eluting on the Chromosil 330/FPD combination. Many interfering compounds have retention times very close to those of the target analytes, and positive identification cannot be made on the basis of retention time

alone. The low molecular weight analytes are usually free of interferences with the exception of carbonyl sulfide. Spikes are sometimes necessary to confirm its identity on the Chromosil 330/FPD side. In some samples, a large concentration of a condensable gas will give rise to pressure surges which will shift the retention times of the early eluting peaks. A spike will be necessary to confirm their identities in this case.

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Since the target compounds can exist in any combination, concentration range and/or ratio, it is impractical to make up a spiking mixture corresponding to each sample. A standard spiking mixture can be made up which contains all of the standard compounds. "Overspiking" (where a standard is added to a sample that has previously been loaded on a cryogenic trap) with compounds not in the sample is desirable as they can be used to determine whether the spike recovery is quantitative.

Use a quantity of spike approximately equal to the amount of the target compound measured. If there is a wide range of apparent analyte concentrations, use a quantity approximately midway between the highest and lowest concentrations of the target analytes.

9.4 Analyte identification. The primary identifying characteristic of the target analytes is their retention time on each of the columns. These are listed in Table I. Note that the retention times will vary somewhat. While the C1-C2 mercaptans elute with very few interfering compounds, the heavier compounds normally elute in a region with many interfering peaks. "Overspiking" is usually necessary for positive identification of these. In some cases, it may be advantageous to switch detectors so that Chromosil 330 effluent goes to the HECD and XE-60 effluent goes to the FPD. Since the two detectors operate on different physical principles and have different interferences, a positive response on both detectors can be taken as a positive confirmation. Detector switching may be useful when a dirty sample is being run which gives many peaks in the region of the target analyte and an overspike does not unambiguously determine peak identity.

The lighter compounds are normally confirmed by the observation of a positive response on both column/ detector combinations. The calculated concentrations of the analyte on both detectors should agree reasonably well. However, because dimethyl sulfide co-elutes with ethyl mercaptan on the Chromosil 330 column, the calculated concentrations of dimethyl sulfide may not agree on the two detectors. If the calculated concentrations do not agree for any of the other components, an interference should be suspected and an overspike may be necessary.

In some instances, a positive response will be seen on one column and not the other. Since at very low concentration levels, the HECD is more sensitive than the FPD, it is possible that a compound could be observed in the XE-60/HECD combination but not on the Chromosil 330/FPD. This will usually occur at the sub-ppb V/V level. Since the heavier compounds are normally measured on the Chromosil 330/FPD only, an overspike is used to provide confirmation rather than relying on dual-column observation.

10. Precision and Accuracy

- 10.1 No precision or accuracy data are currently available in the literature.
- 10.2 Repetitive injections of a known standard on the Chromosil 330/FPD side over a two month period indicate that long-term reproducibility on the FPD is approximately 20%. Back-to-back injections of standards are normally reproducible to 1-2%.
- 10.3 This analytical method was developed at the JWPCP Water Quality Laboratory.

11. References

- 1. Glaser, J.A., Foerst, D.L., McKee, G.D., Quave, S.A., and Budde, W.L., *Environ. Sci. Technol,* 1981, 15, 1426.
- 2. ACS Subcommittee on Environmental Analytical Chemistry, *AnaL Chem.,* 1980, 52, 2242.

TABLE I

Volatile Sulfur Compounds Analyzed by Gas Chromatography

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dimethvl disulfide

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1203A: GAS CHROMATOGRAPHIC ANALYSIS OF AIR, METHANE AND CARBON DIOXIDE USING A PACKED COLUMN

INTRODUCTION

Permanent gases are relatively stable gases (oxygen, argon, nitrogen, carbon dioxide, methane and carbon monoxide) present in air. The relative amounts of these light gases provide us with important information regarding aerobic and anaerobic operations at District facilities and nearby areas. Additionally, permanent gas analyses can be used as screens to give laboratory personnel an approximate volume to inject on other gas chromatographs when trace levels of volatile organics are to be analyzed. Samples are analyzed for permanent gases by packed column chromatography utilizing thermal conductivity detection (TCD). The detector signals are collected by a data system for identification and quantitation of the sample components.

Procedure 1203A: Gas Chromatographic Analysis of Air, Methane, and Carbon Dioxide Using a Packed Column (12-26-91)

1. Scope and Application

This instrumental procedure is to be used for the identification and quantitation of air, methane, and carbon dioxide. Digester gas, engine exhaust, flare exhaust, and landfill gas have been analyzed using this procedure.

- 2. Summary of Procedure
	- 2.1 The sample is injected directly onto a packed column with a 1.0 mL gas-tight syringe.
	- 2.2 The gas chromatograph is operated isothermally to separate the components and TCD is used for component detection.
- 3. Sample Handling
	- 3.1 Samples are collected in the field in either glass bulbs or aluminized, Mylar-coated bags equipped with screw valves or Tedlar (polyvinylfluoride) bags equipped with screw valves.
	- 3.2 Glass bulbs are flushed with laboratory air prior to sampling and are then evacuated. One end of the bulb is connected to the sampling port and both stopcocks are opened. The sample is allowed to purge the bulb for 30 to 60 sec. The stopcocks are then closed and the sample is transported to the laboratory for analysis.
	- 3.3 Aluminized or Tedlar bags are evacuated in the laboratory prior to use. The screw valve is opened and connected to the sampling port. The bag is then allowed to fill under pressure. The valve is closed and disconnected from the sampling port.
	- 3.4 Samples are to be analyzed within 48 h.

4. Apparatus

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- 4.1 Gas Chromatograph
	- 4.1.1 Varian 3400 Series gas chromatograph equipped with thermal conductivity detectors.
	- 4.1.2 Packed column: 2m x 2mm Pyrex packed with 80/100 mesh Porapak QS (Alltech Associates, Inc.).
- 4.2 Data System
	- 4.1.1 Nelson Analytical (3000 series) chromatography software system based on an IBM AT or PS/2 personal computer with a two channel capacity buffer box (760 series) to collect the raw data from the TCD. The data system draws baselines and identifies components according to the software and preselected parameters. The data may be recalculated by the operator by changing the drawn baselines.
	- 4.1.2 Permgas.Bas is a basic program written using the BASIC interpreter. This program is designed to calculate the oxygen and argon concentrations using the CyAr concentration obtained from the Nelson data system. See 7.3 and 7.4. It also averages the methane results from the two permanent gas methods and sums the components for a total permanent gas concentration.
- 4.3 Syringes

One mL glass Pressure-Lok Series A-2 syringes equipped with a Teflon plunger and push-button valve (Precision Scientific) are used.

- 5. Procedure
	- 5.1 Set the gas chromatograph to the following parameters:
		- 5.1.1 Carrier grade Helium (99.9995% purity) at SO mL/min.
		- 5.1.2 Injector temperature: 110 C.
		- 5.1.3 Column temperature: 60 C isothermal.
		- 5.1.4 Detector temperature: 110 C.
	- 5.2 Set the thermal conductivity detector as follows:
		- 5.2.1 Carrier grade Helium (99.9995% purity) reference gas at SO mL/min.
		- 5.2.2 Filament temperature: 130 C.
- 5.2.3 Filament current: 220 mA.
- 5.2.4 Detector polarity: Positive.
- 5.2.5 Detector initial range: 0.5
- 5.5.6 Detector initial attenuation: 8
- 5.5.7 TCD autozero on: YES
- 5.3 Ready the data system for Nelson data collection prior to the start of the run.
- 5.4 Inject 1.0 mL of standard or sample onto the column of the gas chromatograph.
- 5.5 After a 2.0 min analysis, analytes are quantitated by the data system.
- 6. Standards
	- 6.1 A standard calibration is performed each day a sample is run. Linearity studies indicate that the TCD response to these compounds is quite linear over the concentration ranges shown in Table 1. All samples currently analyzed using this method fall within these concentration ranges.
	- 6.2 An air blank is run each day before the standard. This blank is used to determine the amount of contamination of air due to the syringe technique and to insure that the standard line is not contaminated with air. The standard line should be purged for 30 seconds. The pressure in the line should then be adjusted to between 1 and 5 PSI. One mL of the CH₄/CO₂ standard is then drawn and injected. The area count for Air must be below 1,000 before proceeding. This blank value is entered into the calibration curve.
	- 6.3 The syringe is filled with 0.50 mL of a 63.8% CH₄ and 36.3% CO₂ mix (Scott Specialty Gases), and it is then diluted with 0.50 mL of desiccated laboratory air. The air is desiccated by drawing laboratory air through a glass tube filled with silica gel desiccant. This mix is then injected as a standard. If the results obtained are 97% to 103% of the theoretical values (as compared to the previous calibration standard), the standard run is accepted for the calibration standard. If the results are not within this range, two or three standard injections are performed. If the results still fall out of range, trouble-shooting procedures are initiated.
- 7. Calculations
	- 7.1 The data system identifies and quantifies sample components
	- 7.2 Two-point calibration curves (point-to-point) are established for each component using the Nelson data system.

7.3 Air, methane, and carbon dioxide are calculated by the data system as follows:

amount of component (%) = (std amt (%)-blank amt) x sample area in sample (std area-blank area)

The blank value is determined for air only. Blank areas and amounts are assumed to be zero for methane and carbon dioxide.

- 7.4 Values below the method detection limit (MDL) are reported as less than the MDL value. See Table 1. Three significant figures are used for reporting data. Figures past the decimal place of the MDL are not used.
- 8. Quality Assurance Guidelines
	- 8.1 Method detection limits have been established per US EPA Appendix B to Part 136-Definition and Procedure for the Determination of the Method Detection Limit-Revision 1.11. 40 CFR Part 136, 43430, *Federal Register,* Volume 49, No.209. Method detection limits and acceptable linear ranges are presented in Table 1.
	- 8.2 Duplicate injections are performed 10% of the time.
	- 8.3 Duplicate sample analyses are performed 10% of the time if extra sampling can be scheduled.
- 9. Precision and Accuracy

There is no data available at this time for precision and accuracy.

10. References

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This procedure is similar to that published by Supelco, Inc., Analyzing Mixtures of Permanent Gases and Light (C₁-C₁) Hydrocarbons on a Single GC Column, GC Bulletin 712F, Supelco, Inc., Bellefonte, PA, 19S3.

Table 1. Method Detection Limits (MDLs), Linear Ranges (% V/V) and Linear Correlation Coefficients for Permanent Gases Analyzed using Porapak QS and TCD detection (11-9-89).

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600C: GAS CHROMATOGRAPHIC ANALYSIS OF ACETONITRILE IN AIR AND GAS SAMPLES USING A PACKED COLUMN

INTRODUCTION

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Acetonitrile is analyzed by packed column gas chromatography with a flame ionization deteclor (FID). The detector signal is collected by a data system for identification and quantitation of acetonitrile.

Procedure 600C: Analysis of Acetonitrile in Air And Gas Samples (Jan 2.1992)

- 1. Scope and Application
	- 1.1 This instrumental procedure is to be used for the identification of acetonitrile.
	- 1.2 Ambient air, flare exhaust, landfill surface gas, landfill boundary probe, digester gas, landfill gas, engine exhaust and other sample types are analyzed according to this procedure.
- 2. Summary of Procedure
	- 2.1 The sample is injected, cryogenically trapped and thermally desorbed onto a cooled gas chromatographic column.
	- 2.2 The gas chromatograph is temperature programmed to separate the components. The FID detector is used to analyze acetonitrile.
- 3. Sample Handling and Preservation
	- 3.1 Tedlar (polyvinylfluoride) sample bags are bought commercially. The bags are filled with ultrapure nitrogen, allowed to sit overnight, flushed and filled again. This process is repeated ten or more times and then a sample of the blank nitrogen in the bag is analyzed after remaining in the bag overnight. At least two bags from every lot of ten are randomly selected to represent the lot. If the two bags are clean, then the entire set is placed in service. The new bag data is compared to previous lots of new bags to determine acceptability. If the bags are contaminated, they are returned for another round of flushing with ultrapure nitrogen and tested again for suitability.
	- 3.2 Tedlar sample bags are leak checked after each use. Each sample bag is filled with ultrapure nitrogen and allowed to sit overnight with a weight on it. If the bag's volume is reduced significantly, the bag is either repaired or discarded.
	- 3.3 After leak checking, the Tedlar sample bags are cleaned. Each bag is flushed and filled three times with ultrapure nitrogen and allowed to sit overnight. This is repeated two more times and then the bag is returned to service.
- 3.4 The Tedlar sample bags are dedicated for specific sample type and segregated for storage to avoid contamination. Presently we have four sample bag types:
	- 3.4.1 Ambient air bags for ambient air, landfill surface gas,
		- landfill boundary probes, and flare exhaust samples.
	- 3.4.2 Raw bags for raw digester and landfill gas.
	- 3.4.3 Scrubber bags for sewer gas.
	- 3.4.4 Scrubber exhaust bags for exhaust from sewer gas scrubbers.
- 3.5 Samples are collected in the field in Tedlar bags and transported to the laboratory in cardboard boxes to minimize photochemical decomposition. Sample bags are flushed with ultrapure nitrogen (either in the laboratory or the field office) just prior to sample collection.
- 3.6 Samples must be analyzed within 72 hours, but are normally analyzed the day of sampling or the next day.
- 4. Apparatus
	- 4.1 Gas Chromatography
		- 4.1.1 Varian 6000 gas chromatograph equipped with a flame ionization detector connected to column B.
		- 4.1.2 Column: 2 m x 2 mM ID Pyrex packed with 60/80 mesh Carbopack B coated with 1% SP-1000.
		- 4.1.3 Operating parameters:

Reaction gas for FID: Fuel gas: Hydrogen (Ultra high purity), 25 mL/min. Oxidant: Hydrocarbon free air, 300 mL/min. Carrier gas: Helium (carrier grade), 25 mL/min Sweep gas: Helium (carrier grade), 40 mL/min Injector temperature: 150 C Detector base temperature: 300 C for GC 1 and 200 C for GC2 Range 10E-12 for FID Temperature program for GC 1: A 10-min hold at an initial temperature of -99 C. Program to 40 C at 40 C/min and hold for 5 min. Program to 220 C at 8 C/min and hold for 14 min. Temperature program for *GC 2:* Hold 11 min at -20 C. Program to 30 C at 10 C/min and hold for 12 min then program to 65 C at 8 C/min and hold for 12 min. Program to 170 C at 20 C/min and hold for 5 min. Program to 220 C at 40 C/min and hold until all components have eluted.

- 4.2 Data System:
	- 4.2.1 Nelson Analytical (3000 series) chromatography software system based on an

IBM AT or PS/2 personal computer with a two channel capacity buffer box (760 series) to collect the raw data from the FID. The data system draws baselines and identifies components according to the software and preselected parameters. The data may be recalculated by the operator by changing the drawn baselines.

- 4.2.2 NWA Quality Analyst version 3.1 statistical program for quality control charting and analysis.
- 4.2.3 Analytical Automation Specialists AUTOSQC software package which integrates Nelson Analytical 3000 software with NWA Quality Analyst to provide Shewhart quality control charts from chromatographic data.
- 4.2.4 "Limitgcl" and "SP1L20" are basic programs written using the BASIC interpreter. "Limitgcl" is designed to set up tables with component names and calculated acceptable area count range for these components and then produce a hard copy of these tables. "SP1L20.bas" is a basic program that is used to check the daily 100 mL standard injection. Lines 10-330 were modified from Nelson Analytical's "User.Bas" program. "SPlL20.Bas" imports ASCII data from previously saved area tables, compares the proper areas with the limits set up by "Limitgcl.Bas", and prints an exception report listing all compounds that exceed the limit.
- 4.3 Strip Chart Recorder: Linear Instruments Model 282/MM with dual pens.
- 4.4 Cryotrap System
	- 4.4.1 Plumbing: 1/8" nickel tubing kept at approximately 200 using 3/16" nichrome wire heating cord controlled by a Glas-Col Model PL-312 Minitrol voltage regulator set at 2.
- 4.5 Sample Loading System
	- 4.5.1 A 100 mL glass syringe with a Teflon plunger is used to measure the larger sample volumes. Volumes less than 100 mL are loaded onto the cryotrap by injecting the volume through a septum with a gas tight syringe.
	- 4.5.2 Trap utilizing 1/4" ID nickel tubing in a "U" configuration packed with silanized glass beads. The trap is wrapped with 3/16" nichrome wire heating cord controlled by a Glas-Col Model PL-312 Minitrol temperature controller. The trap can be heated to approximately 400 C. Trap B is used for the column connected to the FID (side B).
- 5. Reagents

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5.1 Standard mixture was obtained from Scott-Marrin.Inc. in a cylinder at nominal concentrations of 100 ppb V/V in nitrogen. Table I shows the components in the Scott-Marrin standard currently in use and their concentrations. Working standard is prepared by transferring a volume of 100 ppb V/V standard to a Tedlar bag. See Table II for components and concentrations.

- 6. Procedure
	- 6.1 The data collection method is loaded into the interface box prior to the start of the run. The data collection method instructs the data system how to acquire the data to be generated during the run (i.e. during what times and at what rate the data should be collected). The data system controls all valves through timed event relays.
	- 6.2 The cryotrap is immersed into a liquid nitrogen bath for 1 min prior to sample trapping. The valve actuator is placed in the load position. This allows the helium sweep gas to flow through the cryotrap systems and maintains helium carrier flow through the column.
	- 6.3 A gaseous sample of up to 500 mL is loaded onto the cryotrap side B with a gas tight syringe. The sweep gas carries sample onto the cryotrap.
	- 6.4 The gas chromatograph oven should be cooled: to -99 C and ready for injection.
	- 6.5 Three min after the gas sample has been loaded onto the cryotrap, the liquid nitrogen bath is removed. After waiting 15 sec (to allow the CO2 and NOx to vent) the run is started.
	- *6.6* When the run is started several electrically controlled events occur. The valve controlling the sample flow is switched to "inject", allowing helium sweep gas to carry the sample from the trap to the gas chromatograph column. The cryotrap is heated to approximately 400 C for 4 min and then allowed to cool for 3 min while sweeping sample from the trap onto the column. At the end of this sequence the sample valve is switched back to "load".
	- 6.7 Periodically, 10-point calibration curves are generated for the FID detector. The lifetime of this curve is determined by detector performance. Retention time is updated on a daily basis.

7. Calculations

- 7.1 The data system identifies and quantifies sample components.
- 7.2 Ten-point calibration curve (point-to-point) is established for acetonitrile. A correction factor may be applied if the daily response is found to vary by more than 20% from when the calibration curve was established.

7.3 The peaks that are identified are calculated by the data system as follows:

Cone, of sample = sample peak area x ppb std x mLs of std in ppb, V/V sample Vol, mLs std area x correction factor (if needed) $correction factor = calibration curve area count$ daily standard area count

8. Quality Assurance

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- 8.1 The acceptability of the calibration curve is monitored by injecting 100 mL of the Scott-Marrin gas standard each day the gas chromatograph is used. The area count from the standard is entered into the AUTOSQC statistical program. If the daily standard does not meet the statistical criteria, then corrective action is taken.
- 8.2 Weekly QA includes trip blanks (Tedlar bags filled with ultrapure nitrogen that travel with sample bags to the sampling destination and back to the laboratory for analysis), duplicate samples from the sampling site, and duplicate injections of the same sample (to validate laboratory precision).
- 8.3 Method detection limits have not been documented. Presently a "quantitation limit" is used where a value is not reported if the signal is lower than the lowest signal used in the calibration curve. Quantitation limits are raised when high blank values are found. Typical values are listed in Table I, for both landfill gas (0.5 mL) and ambient air (500 mL) injection volumes.
- 8.4 Sample spiking techniques have not been established.

Table I - Component Currently Analyzed Using FID Cryotrap Method, Test Code and the Current Limits of Quantitation in ppb V/V.

Table II - Scott-Marrin Standard Currently Used And Its Concentrations.

Scott-Marrin Standard I

600B: GAS CHROMATOGRAPHIC ANALYSIS OF ORGANIC COMPOUNDS IN AIR AND GAS SAMPLES USING A PACKED COLUMN

INTRODUCTION

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Volatile organic compounds are analyzed by packed column gas chromatography with a photoionization detector (PID) in series with a Hall electrolytic conductivity detector (HECD). The detector signals are collected by a data system for identification and quantitation of the sample components.

Procedure 600B: Analysis of Oreanic Compounds in Air and Gas (Jan 2. 19921

- 1. Scope and Application
	- 1.1 This instrumental procedure is to be used for the identification and quantitation of volatile organic compounds. The components currently analyzed by this method and their test codes are listed in Table I.
	- 1.2 Ambient air, flare exhaust, landfill surface gas, landfill boundary probe, digester gas. landfill gas, engine exhausts and other sample types are analyzed according to this procedure.
- 2. Summary of Procedure
	- 2.1 The sample is injected, cryogenically trapped and thermally desorbed onto a cooled gas chromatographic column.
	- 2.2 The gas chromatograph is temperature programmed to separate the components. Aromatics and unsaturated hydrocarbons are analyzed using the PID. The effluent from the PID is analyzed for halocarbons by HECD.
- 3. Sample Handling and Preservation
	- 3.1 Tedlar (polyvinylfluoride) sample bags are bought commercially. The bags are filled with ultrapure nitrogen, allowed to sit overnight, flushed and filled again. This process is repeated ten or more times and then a sample of the blank nitrogen in the bag is analyzed after remaining in the bag overnight. At least two bags from every lot of ten are randomly selected to represent the lot. If the two bags are clean, then the entire set is placed in service. The new bag data is compared to previous lots of new bags to determine acceptability. If the bags are contaminated, they are returned for another round of flushing with ultrapure nitrogen and tested again for suitability.
	- 3.2 Tedlar sample bags are leak checked after each use. Each sample bag is filled with ultrapure nitrogen and allowed to sit overnight with a weight on it. If the bag's volume is reduced significantly, the bag is either repaired or discarded.
	- 3.3 After leak checking, the Tedlar sample bags are cleaned. Each bag is flushed and

filled three times with ultrapure nitrogen and allowed to sit overnight. This is repeated two more times and then the bag is returned to service.

- 3.4 The Tedlar sample bags are dedicated for specific sample type and segregated for storage to avoid contamination. Presently we have four sample bag types:
	- 3.4.1 Ambient air bags for ambient air, landfill surface gas, landfill boundary probes, and flare exhaust samples.
	- 3.4.2 Raw bags for raw digester and landfill gas.
	- 3.4.3 Scrubber bags for sewer gas.
	- 3.4.4 Scrubber exhaust bags for exhaust from sewer gas scrubbers.
- 3.5 Samples are collected in the field in Tedlar bags and transported to the laboratory in cardboard boxes to minimize photochemical decomposition. Sample bags are flushed with ultrapure nitrogen (either in the laboratory or the field office) just prior to sample collection.
- 3.6 Samples must be analyzed within 72 hours, but are normally analyzed the day of sampling or the next day.
- 4. Apparatus
	- 4.1 Gas Chromatography
		- 4.1.1 Varian 6000 gas chromatograph equipped with a 10.2 eV HNu model PI-52-02 photoionization detector in series with a Hall model 700A electrolytic conductivity detector (Tracor) operated in the halogen mode.
		- 4.1.2 Column: 2 m x 2 mM ID Pyrex packed with 60/80 mesh Carbopack B coated with *1%* SP-1000.
		- 4.1.3 Operating parameters:

Carrier gas: Helium (carrier grade), 25 mL/min Sweep gas: Helium (carrier grade), 40 mL/min Injector temperature: 150 C Detector base temperature: 300 C Range: 10 for PID and HECD HECD electrolyte: n-propanol at 0.5 mL/min Temperature program: A 10-min hold at an initial temperature of -99 C. Program to 40 C at 40 C/min and hold for 5 min. Program to 220 C at 8 C/min and hold for 14 min.

- 4.2 Data System:
	- 4.2.1 Nelson Analytical (3000 series) chromatography software system based on an

IBM AT or PS/2 personal computer with a two channel capacity buffer box (760 series) to collect the raw data from both PID and HECD. The data system draws baselines and identifies components according to the software and preselected parameters. The data may be recalculated by the operator by changing the drawn baselines.

- 4.2.2 NWA Quality Analyst version 3.1 statistical program for quality control charting and analysis.
- 4.2.3 Analytical Automation Specialists AUTOSQC software package which integrates Nelson Analytical 3000 software with NWA Quality Analyst to provide Shewhart quality control charts from chromatographic data.
- 4.2.4 "Limitgcl" and "SP1L20" are basic programs written using the BASIC interpreter. "Limitgcl" is designed to set up tables with component names and calculated acceptable area count ranges for these components and then produce a hard copy of these tables. "SPlL20.bas" is a basic program that is used to check the daily 50 mL standard injection. Lines 10-330 were modified from Nelson Analytical's "User.Bas" program. "SP1L20.bas" imports ASCII data from previously saved area tables, compares the proper areas with the limits set up by "Limitgcl.bas", and prints an exception report listing all compounds that exceed the limit.
- 4.3 Strip Chart Recorder: Linear Instruments Model 282/MM with dual pens for PID and HECD.
- 4.4 Cryotrap System

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- 4.4.1 Plumbing: 1/8" nickel tubing kept at approximately 200 °C using 3/16" nichrome wire heating cord controlled by a Glas-Col Model PL-312 Minitrol voltage regulator set at 2.
- 4.4.2 1/16" ID Nafion tubing leading from the trap to a stainless steel Valco E60 injection valve. The Nafion tubing (a perfluorinated monomer membrane) is available from Perma Pure Products. Inc., Oceanport, N.J. Water vapor is selectively diffused through the membrane (References 1 and 2).
- 4.5 Sample Loading System
	- 4.5.1 A 100 mL glass syringe with a Teflon plunger is used to measure the larger sample volumes. Volumes less than 100 mL are loaded onto the cryotrap by injecting the volume through a septum with a gas tight syringe.
	- 4.5.2 Trap utilizing 1/4" ID nickel tubing in a "U" configuration packed with silanized glass beads. The trap is wrapped with 3/16" nichrome wire heating cord controlled by a Glas-Col Model PL-312 Minitrol temperature controller. The trap can be heated to approximately 400° C.

5. Reagents

- 5.1 A 1,3-butadiene and benzyl chloride standard mixture was obtained in a Scott "Aculife" polished aluminum cylinder from Scott Specialty Gases with nitrogen as a balance gas. Working standards are prepared by transferring a volume of 100 ppb V/V nominal standard to a Tedlar bag. See Table III for concentrations.
- 5.2 Standard mixtures were obtained from Scott-Marrin, Inc. in cylinders at nominal concentrations of 100 ppb V/V in nitrogen. Table II shows the components in the three Scott-Marrin standards currently in use and their concentrations. Working standards are prepared by transferring a volume of 100 ppb V/V standard to a Tedlar bag.
- 5.3 Quality assurance standards obtained from the National Institute of Standards and Technology (NIST) at nominal concentrations of 250 and 5.0 ppb V/V. The components and concentrations of the nominal 250 ppb V/V standards are listed in Table *TV* and the nominal 5.0 ppb V/V standards are listed in Table V. NIST gas standards are certified for 2 years.

6. Procedure

- 6.1 The data collection methods are loaded into the interface boxes prior to the start of the run. The data collection method instructs the data system how to acquire the data to be generated during the run (i.e. during what times and at what rate the data should be collected). The data system controls all valves through timed event relays.
- 6.2 The cryotrap is immersed into a liquid nitrogen bath for 1 min prior to sample trapping. The valve actuator is placed in the load position. This allows the helium sweep gas to flow through the cryotrap system and maintains helium carrier flow through the column.
- 6.3 A gaseous sample of up to 500 mL is loaded onto the cryotrap with a gas tight syringe. The sweep gas carries sample onto the cryotrap.
- 6.4 The gas chromatograph oven should be cooled to -99 C and ready for injection.
- 6.5 Three min after the gas sample has been loaded onto the cryotrap, the liquid nitrogen bath is removed. After waiting 15 sec (to allow the CO2 and NOx to vent) the run is started.
- 6.6 When the run is started, several electrically controlled events occur. The valve controlling the sample flow is switched to "inject", allowing helium sweep gas to carry the sample from the trap to the gas chromatograph column. The cryotrap is heated to approximately 400 C for 4 min and then allowed to cool for 3 min while sweeping sample from the trap onto the column. At the end of this sequence the sample valve is switched back to "load".
- 6.7 Periodically, 10-point calibration curves are generated for each detector. The lifetime

of these curves is determined by detector performance. Retention times are updated on a daily basis.

- 7. Calculations
	- 7.1 The data system identifies and quantifies sample components.
	- 7.2 Ten-point calibration curves (point-to-point) are established for each detector and component. Correction factors may be applied if the daily response is found to vary by more than 20% from when the calibration curve was established.
	- 7.3 The peaks that are identified are calculated by the data system as follows:

Cone, of sample = sample peak area x ppb std x mLs of std in ppb, V/V sample Vol, mLs std area

x correction factor (if needed)

 $correction factor = calibration curve area count$ daily standard area count

8. Quality Assurance

- 8.1 The acceptability of the calibration curves are monitored by injecting 50 mL of the Scott-Marrin and the Scott Specialty gas standards each day the gas chromatograph is used. The area counts from the standards are entered into the AUTOSQC statistical program. If the daily standards do not meet the statistical criteria, then corrective action is taken.
- 8.2 Weekly QA includes trip blanks (Tedlar bags filled with ultrapure nitrogen that travel with sample bags to the sampling destination and back to the laboratory for analysis), duplicate samples from the sampling site, and duplicate injections of the same sample (to validate laboratory precision).
- 8.3 Method detection limits have not been documented. Presently a "quantitation limit" is used where a value is not reported if the signal is lower than the lowest signal used in the calibration curve. Quantitation limits are raised when high blank values are found. Typical values are listed in Table I, for both landfill gas (0.5 mL) and ambient air (500 mL) injection volumes.
- 8.4 Sample spiking techniques have recently been established. Spiked samples are run weekly and the data is entered into a data base.
- 8.5 Mixtures obtained from the National Institute of Standards and Technology are run weekly. The results are entered into the AUTOSQC statistical program. If the results do not meet statistical criteria, then corrective action is taken. \mathcal{L} is a set of \mathcal{L}

Table II - Scott-Marrin Standards Currently Used And Their Concentrations.

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Scott-Marrin Standard I

Scott-Marrin Standard II

Scott-Marrin Standard III

Table HI - Scott Specialty Gases Standard

Table TV - High Level NIST Standards Currently Used And Their Concentrations

Halocarbon Standard

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Aromatic Standard

Table V - Low Level NIST Standards Currently Used And Their Concentrations

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APPENDIX B QUALITY ASSURANCE

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Appendix B.I Quality Assurance Program Summary $\bar{\mathcal{A}}$

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QUALITY ASSURANCE PROGRAM SUMMARY AND ARB CERTIFICATION

Carnot ensures the quality and validity of its emission measurement and reporting procedures through a rigorous quality assurance (QA) program. The program is developed and administered by an internal QA Officer and encompasses seven major areas:

- 1. Development and use of an internal QA manual.
- 2. QA reviews of reports, laboratory work, and field testing.
- 3. Equipment calibration and maintenance.
- 4. Chain of custody.
- 5. Training.
- 6. Knowledge of current test methods.
- 7. Agency certification.

Each of these areas is discussed individually below.

Quality Assurance Manual. Carnot has prepared a QA Manual according to EPA guidelines. The manual serves to document and formalize all of Carnot's QA efforts. The manual is constantly updated, and each member of the Source Test Division is required to read and understand its contents. The manual includes details on the other six QA areas discussed below.

OA Reviews. Carnot's review procedure includes review of each source test report by the QA Officer, and spot check reviews of laboratory and field work.

The most important review is the one that takes place before a test program begins. The QA Officer works closely with Source Test Division personnel to prepare and review test protocols. Test protocol review includes selection of appropriate test procedures, evaluation of any interferences or other restrictions that might preclude use of standard test procedures, and evaluation and/or development of alternate procedures.

Equipment Calibration and Maintenance. The equipment used to conduct the emissions measurements is maintained according to the manufacturer's instructions to ensure proper operation. In addition to the maintenance program, calibrations are carried out on each measurement device according to the schedule outlined by the California Air Resources Board (CARB). The schedule for maintenance and calibrations are given in Tables B-l and B-2. Quality control checks are also conducted in the field for each test program. The following is a partial list of checks made as part of each CEM system test series.

- Sample acquisition and conditioning system leak check.
- 2-point analyzer calibrations (all analyzers)
- 3-point analyzer calibrations (analyzers with potential for linearity errors).
- Complete system calibration check ("dynamic calibration" through entire sample system).
- Periodic analyzer calibration checks (once per hour) are conducted at the start and end of each test run. Any change between pre- and post-test readings are recorded.
- All calibrations are conducted using gases certified by the manufacturer to be $+$ 1 *%* of label value (NBS traceable).

Calibration and CEM performance data are fully documented, and are included in each source test report.

Chain of Custody. Carnot maintains full chain of custody documentation on all samples and data sheets. In addition to normal documentation of changes between field sample custodians, laboratory personnel, and field test personnel, Carnot documents every individual who handles any test component in the field (e.g., probe wash, impinger loading and recovery, filter loading and recovery, etc.).

Samples are stored in a locked area to which only Source Test Division personnel have access. Neither other Carnot employees nor cleaning crews have keys to this area.

Data sheets are copied immediately upon return from the field, and this first generation copy is placed in locked storage. Any notes made on original sheets are initialed and dated.

Training. Personnel training is essential to ensure quality testing. Carnot has formal and informal training programs which include:

- 1. Attendance at EPA-sponsored training courses.
- 2. Enrollment in EPA correspondence courses.
3. A requirement for all technicians to read and
- A requirement for all technicians to read and understand Carnot's QA Manual.
- 4. In-house training and QA meetings on a regular basis.
- 5. Maintenance of training records.

Knowledge of Current Test Methods. With the constant updating of standard test methods and the wide variety of emerging test methods, it is essential that any qualified source tester keep abreast of new developments. Carnot subscribes to services which provide updates on EPA and CARB reference methods, and on EPA, CARB and SCAQMD rules and regulations. Additionally, source test personnel regularly attend and present papers at testing and emission-related seminars and conferences. Carnot personnel maintain membership in the Air Pollution Control Association, the Source Evaluation Society, and the ASME Environmental Control Division.

AGENCY CERTIFICATION

Carnot is certified by the CARB as an independent source test contractor for gaseous and paniculate measurements. Carnot also participates in EPA QA audit programs for Methods 5, 6 and 7.

TABLE B-l SAMPLING INSTRUMENTS AND EQUIPMENT CALIBRATION SCHEDULE As Specified by the CARB

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TABLE B-2 EQUIPMENT MAINTENANCE SCHEDULE Based on Manufacturer's Specifications and Carnot Experience

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Appendix B.2 ARB Certification

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State of California AIR RESOURCES BOARD

Executive Order G-767

Approval to Carnot To Conduct Testing as an Independent Contractor

WHEREAS, the Air Resources Board ("Board"), pursuant to Section 41512 of the California Health and Safety Code, has established the procedures contained in Section 91200-91220, Title 17, California Code of Regulations, to allow the use of independent testers for compliance tests required by the Board; and

WHEREAS, pursuant to Sections 91200-91220, Title 17, California Code of Regulations, the Executive Officer has determined that Carnot meets the requirements of the Board for conducting ARB Test Methods 1, 2, 3, 4, 5, 6, 8, 10, and 100 (NOx, 02) when the following conditions are met:

1. Carnot conducts ARB Test Method 100 for 02 using a Teledyne 226 analyzer with either a A5 or a Bl sensor, or a paramagnetic analyzer.

NOW, THEREFORE, BE IT ORDERED that Carnot is granted an approval, from the date of execution of this order, until June 30, 1993 to conduct the tests listed above, subject to compliance with Section 91200-91220, Title 17, California Code of Regulations.

BE IT FURTHER ORDERED that during the approved period the Executive Officer or his or her authorized representative may field audit one or more tests conducted pursuant to this order for each type of testing listed above.

TV ^ Executed this \sqrt{O} day of $\sqrt{O(1+\frac{O(\epsilon)}{O(\epsilon)}}$ 1992, at Sacramento, California.

James J. Morgester, Chief Compliance Division

Carnot

This is to certify that the company listed above has been approved by the Air Resources Board to conduct compliance testing, pursuant to Section 91207, Title 17, California Code of Regulations, until June 30, 1993, for those test methods listed below:

> ARB Source Test Methods: 1, 2, 3, 4, 5, 6, 8,10,100 (NOx, O2),

James J. Morgester, Chief Compliance Division

H. Roye Jackson, Manager

Field Evaluation Section

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Appendix B.3 Calibration Data $\bar{\gamma}$

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DRY GAS METER CALIBRATION

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CARNOT SPAN GAS RECORD

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ALLOWABLE DEVIATION IS 2% OF FULL SCALE (2 SQUARES ON STRIP CHART).

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Scott Specialty Gases, Inc.

FAX 714-887-0549 PHONE: 714-887-2571

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Contract

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2600 CAJON BLVD., SAN BERNARDINO, CA 92411

CARNOT

ATTN: RICK MADRIGAL 15991 RED HILL AVE **SUITE 110** TUSTIN CA 92680

NITROGEN **BALANCE GAS** ANALYZER READINGS: $Z = Zero Gas$ T = Test Gas

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 $R =$ Reference Gas

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<u>CONTRACTORS</u>

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nALANCE GAS NITROGEN
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Scott Specialty Gases, Inc.

Cariooned a monda

2600 CAJON BLVD. SAH EFREARDIED Phone: 714-887-2521

CA 92411

Fax: 716-887-0549

CERTIFICATE OF ANALYSIS

CARNOT -PROJECT #: 02-22304 ATTN: RICK MADRIGAL PO#: 8957 15991 RED HILL AVE ITEM #: 020203013601AL SUITE 110 DATE: 10/29/92 TUSTIN CA 92400

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Scott Specialty Gases, Inc.

Shipped 2600 CADUN BLVD. SAN EERNARDING Findom #1 Phone: 714-887-2571

CA 92411

Fax: 714-887-0549

CERTIFICATE OF ANALYSIS

CARNOT ATTM: RICK MADRIGAL 15991 RED HILL AVE SUITE 110 TUSTIN

PROJECT #: 02-22304 PO#: 8957 ITEM W: 020203000701AL DATE:10/26/92

CA 92680

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SOUTH PLAINFIELD, NEW JERSEY / FREMONT, CALIFORNIA / WAKEFIELD, MASSACHUSETTS / LONGMONT, COLORADO

Appendix B.4 Chain of Custody

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CHAIN OF CUSTODY

ANALYSIS REQUIRED:

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CARNOT.

15991 Red Hill Ave., Suite 110, Tustin, California 92680-7388 (714) 259-9520 - FAX (714) 259-0372

PML-007

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FIELD PERSONNEL

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LAB PERSONNEL

SAMPLE NO.		$\mathbf{2}$	3	4	5	6	
LOG NO.		951919519295171					
BAG COND. **		₽					
COMMENTS							
SAMPLE RECEIVED BY: WILL C'M. Cully DATE: $12/20/92$ $**$ $F = MORE$ THAN 1/2 FULL $*ATR - AMBIENT ATR$ $\sim 3\,$ μ μ $L = 1/4$ TO $1/2$ FULL ILSS - SURFACE GAS $E = LESS$ THAN 1/4 FULL LFGS - LANDFILL GAS (RAW) BUT CONTAINS SOME STGS - FLARE EXHAUST SAMPLE LPGP - BOUNDARY PROBE $N = NO$ SAMPLE IN BAG							
RETURN THIS FORM TO Moon Chung ARE RECEIVED BY LAB PERSONNEL.						AFTER SAMPLES	

APPENDIX C FIELD AND LAB DATA SUMMARIES

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Appendix C.1 Sample Locations

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CARNOT SAMPLING POINT LOCATION DATA - EPA METHOD 1 PV V_{n} , \vdots \vdots $\rho_{\text{AIA BY:}}$ PLANT: DATE: 12/30/92 S tacle TEST LOCATION:. $\frac{\beta}{\beta}$ $\frac{\beta}{a}$ = 4²
Stack Dia. = 41² ہے
انگر $\overline{\omega}$ 22 ς Diagram of Sampling Location **SAMPLE** %OF IN. FROM IN. FROM POINT NEAR WALL NOZZLE* DIAMETER 32 て γ ϵ **I** UPSTREAM DISTJOIA.: 1.58 **?** 4.3 10.5 9.8 **3 7.9 s** 72 $19, 4$ DOWNSTREAM DISTJOIA: 6.44 **V** 37.3 13.2 /S- 7 COUPLING LENGTH: 5.5 3 $67, 7$ 27.8 37.3 ه) [NO. OF SAMPLING PTS.: $\overline{\mathcal{C}}$ 33.0 38.5 80.6 $\overline{}$ 41 $\overline{4}$ $\overline{2}$, $\overline{2}$ 89.5 7
रु STACK DIMENSION: _ 36.7 9.168 $96,8$ 37,7 452 STACK AREA, FT?: _ •INCHES FROM WALL PLUS COUPLING LENGTH **PM?-002 CARNOT**

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Carnot 13-Jan-93

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CARNOT CEM PERFORMANCE DATA

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CLIENTAOCATION: $PVERG$ DATE: $12-30-92$ BY: CH/F

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CARNOT REFERENCE METHOD GASEOUS MEASUREMENTS

CLIENTAOCATION: PVER6 $12 - 30 - 42$

 $\overleftrightarrow{\mathsf{DATE}}$:

CONDITION: _

 CHF OPERATOR:

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TEST NUMBER: 2-CEM. PV

TEST LOCATION:

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CLIENT/LOCATION:

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 CHF

 $1-CEM-PV$ TEST NUMBER:

TEST LOCATION: Stack

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SOURCE TEST DATA SUMMARY

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SOURCE TEST DATA SUMMARY

Part Emission lb/hr 0.2562

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METHOD OF SAMPLE PREPINOTES **AND THE SECOND ACTION AND RELEASE OF SAMPLE PREPINDENCE**

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Appendix C.4 Inlet Moisture and Calculated Flow Rate Data

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Appendix C.5 Total Hydrocarbon Lab Results

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21354 Nordhoff St., Suite 113, Chatsworth, CA 91311 (818) 718-6070 • FAX (818) 718-9779

environmental consultants laboratory services

January 6, 1993 **LTR/005/93**

Craig Fry
CARNOT $CARNOT$ 15991 Red Hill Ave. Suite 110 JA _i 1 i 993 Tustin, CA 92680

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re: 54700

Dear Craig:

Please find enclosed the laboratory analysis report, quality assurance summary, and the original chain of custody form for four Tedlar bag samples received on December 31, 1992.

The samples were analyzed for methane and total gaseous non-methane organics.

Sincerely,

AtmAA, Inc.

Corechau

Michael L. Porter Laboratory Director

Encl. MLP/krp

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environmental consultants laboratory services

LABORATORY ANALYSIS REPORT

Methane & Total Gaseous Non-Methane Organics Analysis in Tedlar Bag Samples

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ANALYSIS DESCRIPTION

Methane and total gaseous non-methane organics were measured by flame ionization detection/total combustion analysis portion (FID/TCA).

TGNMO is total gaseous non-methane organics measured and reported as ppm methane.

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Michael L. Porter Laboratory Director

QUALITY ASSURANCE SUMMARY *(Repeat Analysis)*

A set of 4 Tedlar bag samples laboratory numbers, 93662-(2-5) was analyzed for methane and TGNMO. Agreement between repeat analyses is a measure of precision and is shown above in the column "% Difference from Mean." Repeat analyses are an important part of AtmAA's quality assurance program. The average % Difference from Mean for 3 repeat measurements from the sample set of 4 Tedlar bag samples is 1.6%.

CARNOT **TEDLAR BAG SAMPLE DATA**

 $PVER6$ CLIENT/PROJECT:

DATE:

 \sim UNIT:

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CARNOT TEDLAR BAG SAMPLE DATA

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DATE: $12 - 30 - 92$ UNIT: $PVERG = 1$
BY: C/HF

DATE: UNIT:. .BY:

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TRACE ORGANIC SPECIES DESTRUCTION EFFICIENCY RESULTS PVERG UNIT 1, TEST No. 1 DECEMBER 30, 1992

ND< - indicates that the species was not detected. Values indicate the detection limit for this species and the concentration is less than the presented value.

NA - indicates that the destruction efficiency cannot be calculated because the concentration is below the detection limits. .

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TRACE ORGANIC SPECIES DESTRUCTION EFFICIENCY RESULTS PVERG UNIT 1, TEST No. 2 DECEMBER 30, 1992

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ND< - indicates that the species was not detected. Values indicate the detection limit for this species and the concentration is less than the presented value.

NA - indicates that the destruction efficiency cannot be calculated because the concentration is below the detection limits.

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PALOS VERDES LANDFILL PVERG BOILER Test Date: 12/30/92

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Appendix C.7 Unit Operation Data \sim

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APPENDIX D **CALCULATIONS**

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Appendix D.I General Emissions Calculations

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EMISSION CALCULATIONS

1. Sample Volume and Isokinetics

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a. Sample gas volume, dscf

$$
V_{m \, sd} = 0.03342 \; V_{m} \left(P_{bar} + \frac{H}{13.6} \right) \left(\frac{T_{ref}}{T_{m}} \right) (Y)
$$

b. Water vapor volume, scf

$$
V_{\text{w sd}} = 0.0472 V_{\text{k}} \left(\frac{T_{\text{ref}}}{528 \text{° R}} \right)
$$

c. Moisture content, nondimensional

$$
B_{\rm wo} = \frac{V_{\rm w \, std}}{V_{\rm m \, std} + V_{\rm w \, std}}
$$

d. Stack gas molecular weight, lb/lb mole

 MW_{dyn} = 0.44 (%CO₂) + 0.32 (%O₂) + 0.28 (%N₂)

 $MW_{wct} = MW_{dry} (1 - B_{w0}) + 18 (B_{w0})$

e. Absolute stack pressure, iwg

$$
P_s = P_{bar} + \frac{P_{sg}}{13.6}
$$

f. Stack velocity, ft/sec

$$
V_{s} = 2.90 \, C_{p} \sqrt{\Delta PT_{s}} \sqrt{\left(\frac{29.92}{p_{s}}\right)\left(\frac{28.95}{MW_{\text{wcl}}}\right)}
$$

g. Actual stack flow rate, wacfm

 $Q = (V)(A)(60)$

h. Standard stack gas flow rate, dscfm

$$
Q_{sd} = Q (1 - B_{\text{two}}) \left(\frac{T_{ref}}{T_s} \right) \left(\frac{P_s}{29.92} \right)
$$

i. Percent isokinetic

$$
I = \left(\frac{17.32(T_{\bullet})(V_{m,\text{rad}})}{(1 - B_{\text{wa}})(\Theta)(V_{\bullet})(P_{\bullet})(D_{n}^{2})}\right) \left(\frac{528 \text{ °R}}{T_{\text{ref}}}\right)
$$

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2. Particulate Emissions

a. Grain loading, gr/dscf

$$
C = 0.01543 \left(\frac{M_n}{V_{m \text{ rad}}}\right)
$$

b. Grain loading at 12% CO₂, gr/dscf

$$
C_{12\%CO_2} = C \left(\frac{12}{\% CO_2}\right)
$$

c. Mass emissions, lb/hr

$$
M = C(Q_{sd}) \frac{(60 \text{ min/hr})}{(7000 \text{ gr/lb})}
$$

3. Gaseous Emissions, lb/hr

$$
M = (ppm)(10^{-6})\left(\frac{MW_i \text{ lb/lb mole}}{SV}\right)(Q_{sd})(60 \text{ min/hr})
$$

where,

SV = *specific molar volume of an ideal gas:*

 $SV = 385.3 \text{ ft}^3\text{/lb mole}$ for $T_{ref} = 528 \text{ }^{\circ}R$

 $SV = 379.5 \text{ ft}^3 \text{/lb mole}$ for $T_{\text{ref}} = 520 \text{ °R}$

- 4. Emissions Rates, lb/10⁶ Btu
	- a. Fuel factor at $68 °F$, dscf/ $10⁶$ Btu at 0% O₂

$$
F_{68} = \frac{10^6 [3.64(\%H) + 1.53(\%C) + 0.14(\%N) + 0.57(\%S) - 0.46(\%O_{2s}fuel)]}{HHV, \text{ Btu/lb}}
$$

b. Fuel factor at $60 °F$

$$
F_{\text{60}} = F_{\text{68}} \left(\frac{520 \text{ }^{\circ} R}{528 \text{ }^{\circ} R} \right)
$$

c. Gaseous Emissions factor

$$
\left(\frac{lb}{10^6 \, Btu}\right)_i = (ppm)_i \, (10^{-6}) \left(\frac{MW_i \, lb}{lb \, mole}\right) \left(\frac{1}{SV}\right) (F) \left(\frac{20.9}{20.9 - \%O_2}\right)
$$

d. Paticulate emission factor

$$
\left(\frac{lb}{10^6 \; Btu}\right) = C\left(\frac{1 \; lb}{7000 \; gr}\right) (F) \left(\frac{20.9}{20.9 - \% O_2}\right)
$$

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Nomenclature:

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Nomenclature (Continued):

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SUBJECT Sample Calculations for Flow Rate, Moisture and Particulate Matter SHEET NO. -COMPUTED BY $C \cdot F \cdot \gamma$ DATE $1 - 18 - 93$ CHECKED BY See Appendix D.I for Test N_0 , $2-pm-PV$ Nomenclature Note: $\alpha v_9 \Delta P = (\epsilon \sqrt{\Delta P})^2$ Vstd = Standard Sample Volume Metered (SCf) V_{m} _{st} = 0.03342 (Vm) $(P_{Bar} + \frac{\Delta H}{13.6})(\frac{Tr_{e}F}{T_{m}})$ $V_{nst} = 0.03342(33.677)(\frac{29.96}{13.6})\frac{520}{(79.78+460)}$ $V_{r,s11} = 32.526$ V_{wstd} = Water Vaper Volume (scf) $V_{wst,i} = 0.0472(V_{k})\left(\frac{T_{ref}}{528.8}\right)$ $V_{W31}J = 0.0472(1200) 520$ $V_{wstJ} = 5.578/8$

15991 RED HILL AVENUE, SUITE 110, TUSTIN, CA 92680-7388 (714) 259-9520 / Telecopy: (714) 259-0372

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SUBJECT Sample Calculations, Continued COMPUTED BY C, Fry DA Ps = Absolute Stack Pressure $P_s = P_{bar} + \frac{P_{s+}}{13.6}$ $P_5 = 29.96 + \frac{t.1181}{13.6}$ $Ps = 29.969$ V_s = Stack Velocity ft/sec $V_s = 2.90(c_{\rho}) \sqrt{\frac{\Delta P}{T_s}} \sqrt{\frac{29.92}{\rho_s}} \sqrt{\frac{28.95}{MW_{wd}}}$ $V_5 = 2.90(.84))\sqrt{(4750)(33675+400)}\sqrt{\frac{29.92}{29.769}}$ $Vs = 2.90(0.84)/(19.4539s)/(1.00736)$ $V_s = 47.738$ Note: Ts = Temp Stack F° + 460

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CARN SUBJECT_Sample Calculations, Continued SHEET NO. 4.5 COMPUTED BY CHECKED BY DATE Q = Stack Flow Rate, Wet actual (wacfm) $Q=(V_s)(A_s)$ 60 section $As = StackArea$ $Q=(47.738)(9.168)60$ $Q = 26259.9$ Qstd = Standard Stack Flow Rate, dscfm $Qstd = Q (1-Bwo)(\frac{Tref}{er})(\frac{f}{2aa}$ $Qsld = 26,2599(1-.146)$ $\frac{520}{460+37675}$ $\frac{29.969}{7997}$ Q stJ = 14660

CARNOT SUBJECT Sample Calculations, Continued **JOB** SHEET NO. S_{off} DATE_ C = particulate grain loading $9^r/sc$ $C = O.01543 \left(\frac{M_{n}}{V_{ms}H}\right)$ $C = 0.01543(\frac{4.30}{32526})$ $C = 0.0020$ $M = Mass$ Emissions $16/hr$ $M = (C)(Q_{11}) \frac{60 \text{min/h}}{7000 \text{ g} \cdot /16}$ $M = 0.0070 14660 x60$ $M = 0.256$

¹⁵⁹⁹¹ RED HILL AVENUE, SUITE 110, TUSTIN, CA 92680-7388 (714) 259-9520 / Telecopy: (714) 259-0372

Appendix C.2 CEM Data and Strip Charts

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