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Office of Air Quality
Planning and Standards
Research Triangle Park, NC 27711

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Air

# LIME MANUFACTURING EMISSIONS TEST REPORT (FOURIER TRANSFORM INFRARED SPECTROSCOPY)

## Chemical Lime Company
## (Formerly Eastern Ridge Lime Company)
## Ripplemead, Virginia

# LIME MANUFACTURING EMISSION TEST REPORT (FOURIER TRANSFORM INFRARED SPECTROSCOPY)

**FINAL REPORT**

Chemical Lime Company
(Formerly Eastern Ridge Lime Company)
Ripplemead, Virginia

Prepared for

Emission Measurement Center
United States Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Attn: Michael L. Toney

EPA Contract NO. 68-D-98-027
Work Assignment 2-11
MRI Project No. 104951-1-011-06

September 30, 1999

## Preface

This report was prepared by Midwest Research Institute (MRI) for the U. S. Environmental Protection Agency (EPA) under EPA Contract No. 68-D-98-027, Work Assignment No. 2-11. Mr. Michael Toney is the EPA Work Assignment Manager (WAM). Dr. Thomas Geyer is the MRI Work Assignment Leader (WAL). The field test was performed, and draft and revised test reports were submitted under EPA Contract No. 68-D2-0165, Work Assignment No. 4-01. Mr. Dennis Holzschuh and Michael Toney were the EPA WAMs for the Emission Measurement Center (EMC) under Work Assignment 4-01.

This report presents the procedures, schedule, and test results for an emissions test performed at Eastern Ridge Lime Company in Ripplemead, Virginia. The field test was conducted in October, 1996. The draft and revised test reports were submitted in January and September 1997, respectively. MRI performed FTIR emissions measurements at the inlet and outlet of a wet scrubber control device using EPA Method 320. Method 320 has since been promulgated in the Federal Register on May 19, 1999.

This report consists of one volume (210 pages) with six sections and five appendices.

Midwest Research Institute

for Andrew Trenholm
Deputy Program Manager

Approved:

for Jeff Shular
Director, Environmental Engineering Division

September 30, 1999

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# 1.0 INTRODUCTION

## 1.1 BACKGROUND

The Emission Measurement Center (EMC) of the U. S. EPA received a request from the Minerals and Inorganic Chemicals Group (MICG) of the U.S. EPA to perform emissions testing at coal-fired lime kilns. In partial fulfillment of the test request, EMC issued Work Assignments 2-11 and 4-01 under EPA Contract Nos. 68-D-98-027 and 68-D2-0165, respectively, to Midwest Research Institute (MRI). The purpose of this project was to measure organic and inorganic hazardous air pollutants (HAPs) using a test method based on Fourier transform infrared (FTIR) spectroscopy. This report describes the test procedures and presents results of the testing at Eastern Ridge Lime plant in Ripplemead, Virginia.

## 1.2 PROJECT SCOPE

Three locations were tested at Eastern Ridge: the inlet and outlet of a wet scrubber off of the kiln, and the hydrator stack.

The procedures followed in this test are described in the FTIR sampling Method 320 for hazardous air pollutants (HAPs).[1] The objectives of the field test were to: (1) screen for HAPs regulated in Title III of the 1990 Clean Air Act Amendments, (2) measure, if detected, compounds that have been previously measured at cement kilns (e.g., formaldehyde, napthalene, p-xylene), and (3) measure other pollutants such as $SO_2$ and $NO_x$.

The test request specifically identified HCl as a target analyte. This facility uses coal as fuel to fire the kiln and HCl has been measured with FTIR methods at other coal-burning facilities. Draft Method 320 (reference 1) uses an analyte spiking procedure for quality assurance (or Method 301 validation) to verify that the sampling system is suitable for measuring target analyte(s) at the expected concentration. In this test, analyte spiking was performed using an HCl cylinder standard from Scott Specialty Gases.

In the FTIR screening procedure, spectra of gas samples contained in a leak tight infrared gas cell are recorded at regular intervals over a sampling run. Typically, 8 to 10 sample spectra are recorded in an hour. These spectra are then analyzed using reference spectra in the EPA library to identify and quantify any HAPs in sample. Unidentified spectral features are analyzed to check for the presence of other compounds, for which there are currently no reference spectra.

## 1.3 PROJECT PERSONNEL

This project was administered by the EMC of the U.S. EPA. The Test Request was initiated by the MICG of the Office of Air Quality and Standards (OAQPS). Midwest Research was assisted in the field test by staff from Emission Testing Services, Inc. (ETS) and Envirostaff, Inc. Dr. Grant Plummer of Rho Squared assisted in the data analysis. Key project personnel are listed in Table 1-1.

TABLE 1-1. PROJECT PERSONNEL

| | | |
|---|---|---|
| Eastern Ridge Lime Company | J. Steven Castleberry | (618) 465-7741 |
| EMC Work Assignment Manager | Mr. Michael Toney | (919) 541-5247 |
| MRI Work Assignment Leader | Dr. Thomas Geyer | (919) 851-8181 |

# 2.0 TEST LOCATIONS

Eastern Ridge Lime Company has two coal-fired rotary kilns. Emissions from the kiln are controlled by two parallel Ducon wet scrubbers.

The facility also operates a hydrator to convert lime to hydrated lime.

The sampling location figures were prepared by Pacific Environmental Services, Inc. (PES). The information below was also provided by PES.

## 2.1 NO. 2 KILN SCRUBBER INLET

The common inlet is in a rectangular duct at a 45° angle to ground. At the kiln discharge the duct is about 6-ft by 4-ft. The dimensions narrow to about 5-ft by 4-ft immediately before the duct splits upstream of the two scrubbers. Insulation was placed over the duct to provide a heat shield.

The scrubber inlet location was within 50-ft of the outlet locations and within 100-ft of where the FTIR trailer was parked. Figure 2-1 is a schematic of this location.

## 2.2 SCRUBBER OUTLETS (A AND B)

The sampling locations at the outlets of both scrubbers were similar. The scrubber outlet stacks were within 8-ft of each other and within 100-ft of the FTIR trailer location. The outlet sampling ports were in 48-in ID, round vertical stacks. Scaffolding and a ladder provided access to ports in the scrubber stacks.

Flow straightening vanes were lowered into each stack before testing. The vanes blocked the original FTIR test ports so new ports were cut in each stack just above the tops of the vanes below the manual sampling ports. Figure 2-2 is a schematic of the scrubber outlet locations.

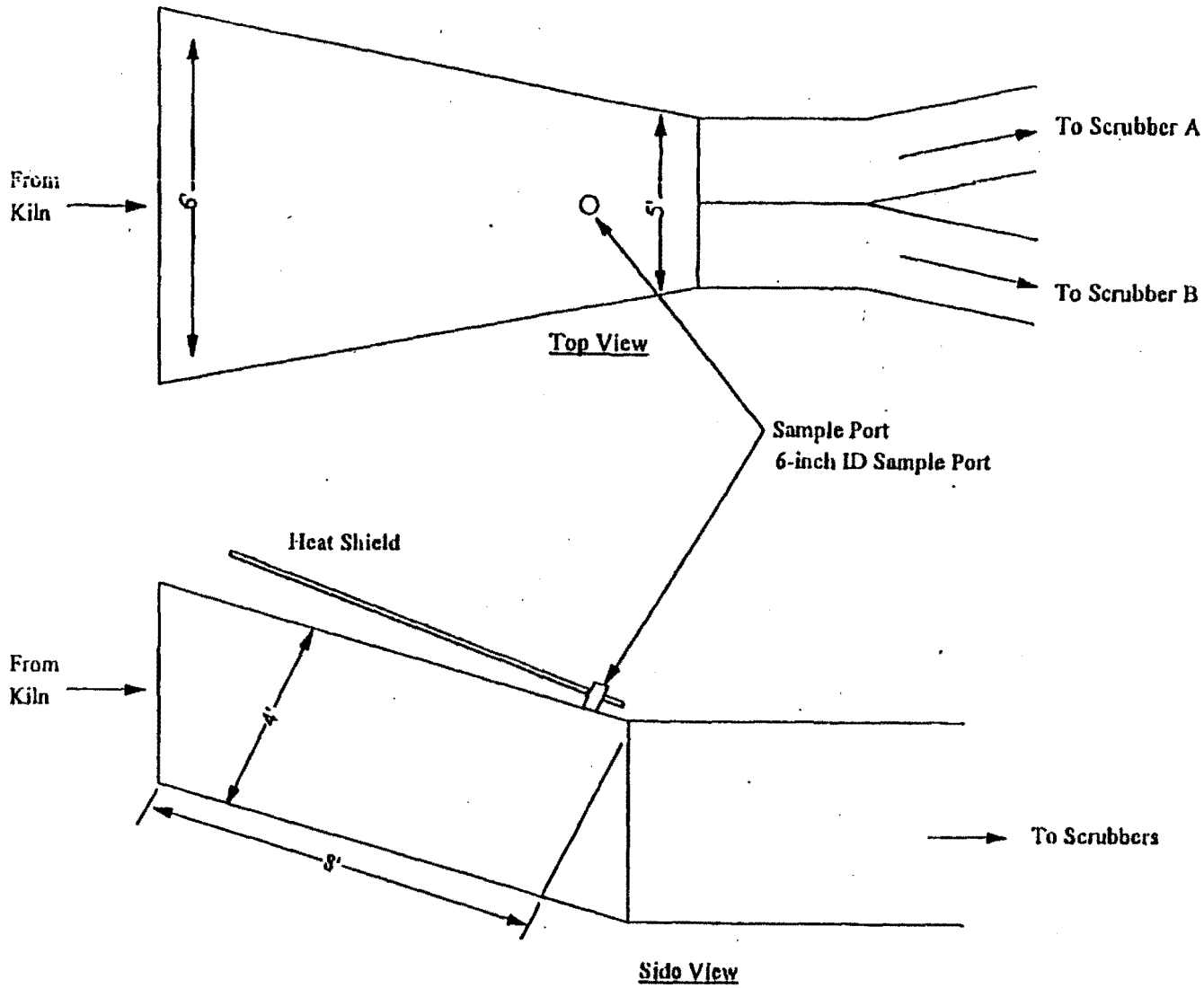
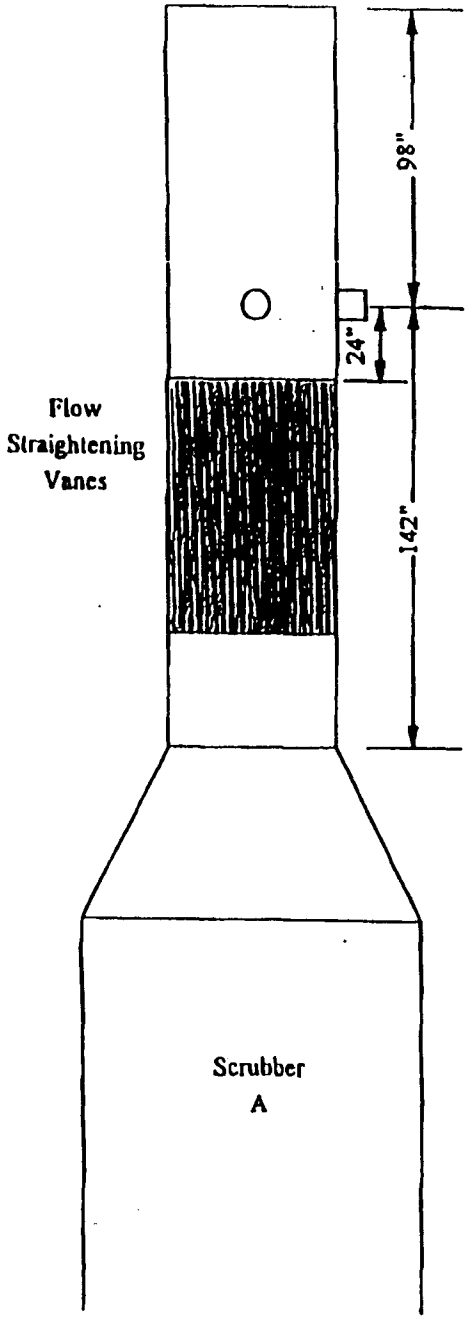
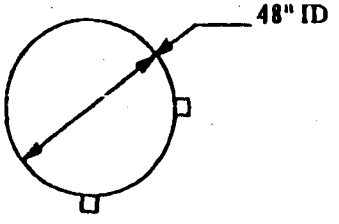



Figure 2-1. Scrubber inlet location.




Cross-Section

SAMPLE TRAVERSE POINT LOCATIONS

| Point Number | Fraction of Stack ID | Distance Inches | Port Depth Inches | Port Location Inches |
|---|---|---|---|---|
| 1 | .021 | 1.00 | 3.25 | 4.25 |
| 2 | .067 | 3.19 | 3.25 | 6.44 |
| 3 | .118 | 5.69 | 3.25 | 8.94 |
| 4 | .177 | 8.50 | 3.25 | 11.75 |
| 5 | .250 | 12.00 | 3.25 | 15.25 |
| 6 | .356 | 17.06 | 3.25 | 20.31 |
| 7 | .644 | 30.94 | 3.25 | 34.19 |
| 8 | .750 | 36.00 | 3.25 | 39.25 |
| 9 | .823 | 39.50 | 3.25 | 42.75 |
| 10 | .882 | 42.31 | 3.25 | 45.56 |
| 11 | .933 | 44.81 | 3.25 | 48.06 |
| 12 | .979 | 47.00 | 3.25 | 50.25 |

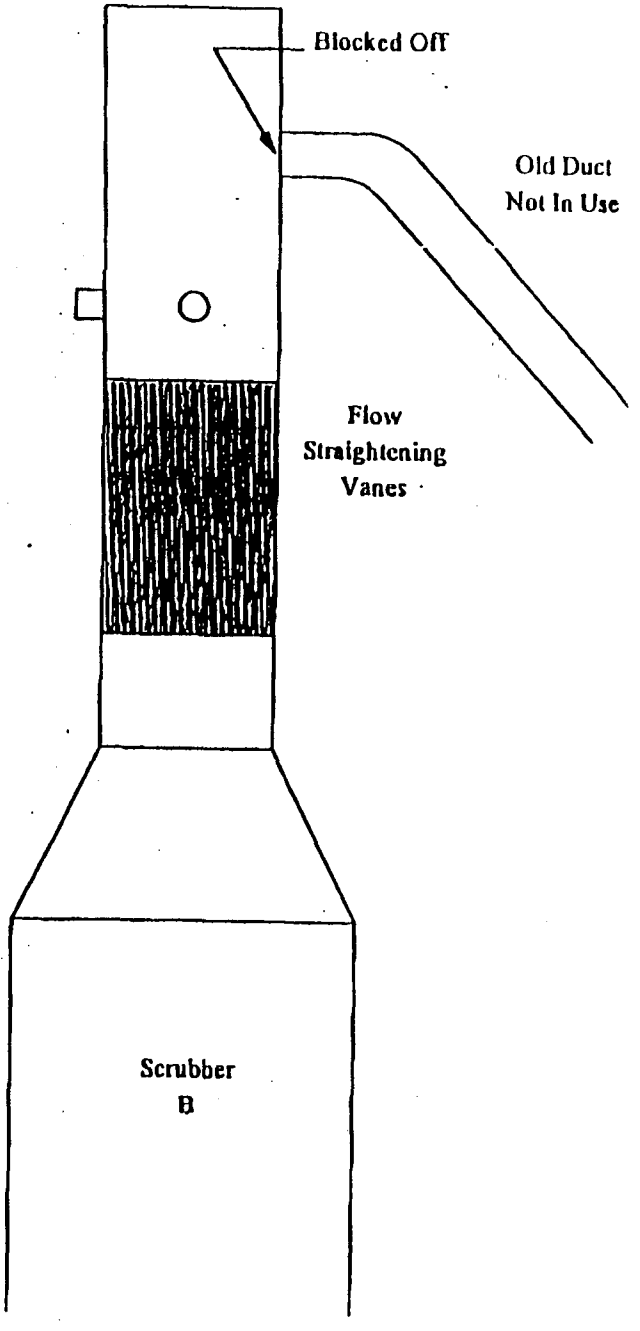
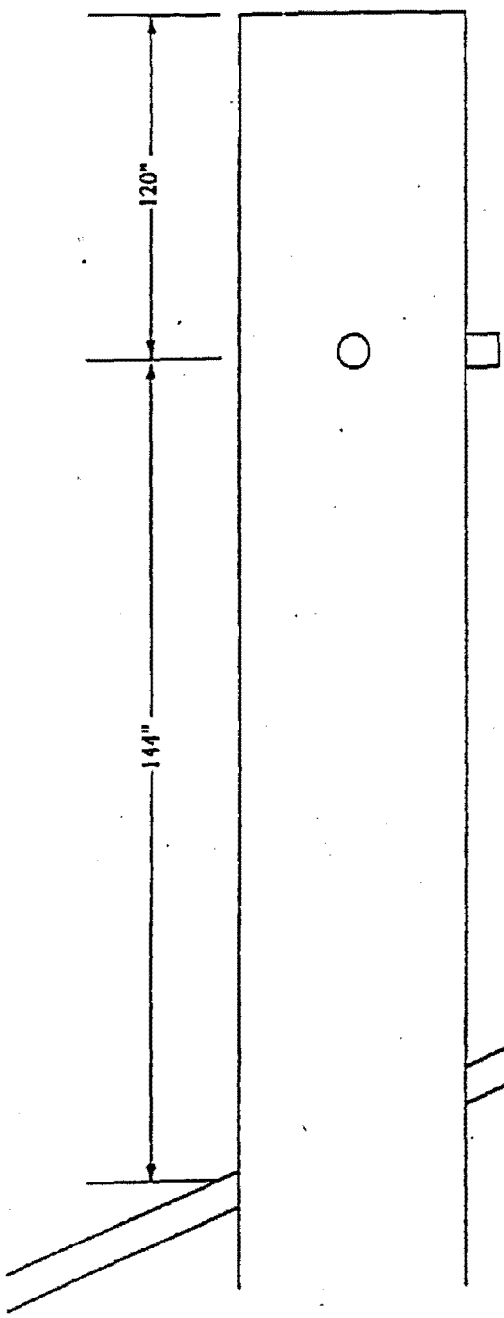


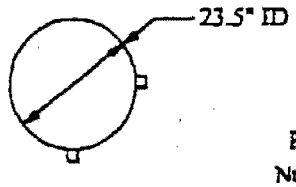

Figure 2-2. Scrubber outlet stacks.

## 2.3 HYDRATOR STACK

The sampling ports were in a (23.5-in ID) round, vertical stack, 10-ft upstream and 12-ft downstream of the nearest flow disturbances. An inside stairway provided access to the roof and scaffolding provided access to the sampling ports. The sampling location was within 100-ft of the FTIR trailer position.

Figure 2-3 is a schematic of the hydrator stack location. The FTIR sampling ports were about 4-ft below the manual sampling ports shown in Figure 2-3.




Cross Section

SAMPLE TRAVERSE POINT LOCATIONS

| Point Number | Fraction of Stack ID | Distance Inches | Port Depth Inches | Port Location Inches |
|---|---|---|---|---|
| 1 | .032 | 0.75 | 3.00 | 3.75 |
| 2 | .105 | 2.44 | 3.00 | 5.44 |
| 3 | .194 | 4.96 | 3.00 | 7.56 |
| 4 | .323 | 7.96 | 3.00 | 10.56 |
| 5 | .677 | 15.94 | 3.00 | 18.94 |
| 6 | .806 | 18.94 | 3.00 | 21.94 |
| 7 | .895 | 21.06 | 3.00 | 24.06 |
| 8 | .968 | 22.75 | 3.00 | 22.75 |

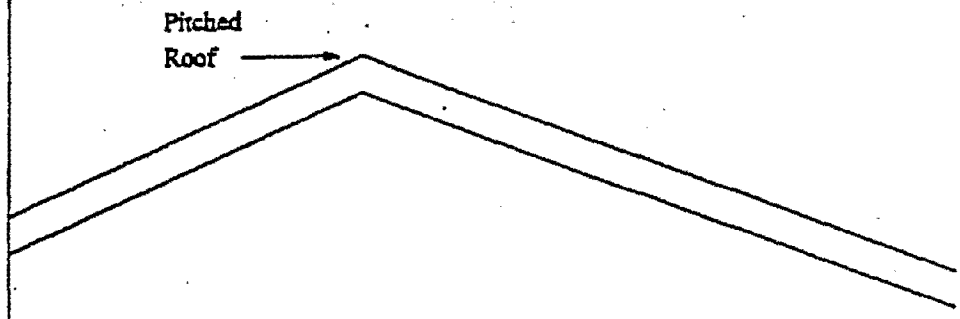



Figure 2-3. Hydrator stack.

# 3.0 RESULTS

## 3.1 TEST SCHEDULE

The testing was completed within a week on the test site from October 14 through October 19, 1996. Table 3-1 summarizes the FTIR sampling schedule. A complete record of all FTIR sampling is in Appendix B.

The FTIR testing was coordinated with manual sampling and Method 25A testing performed by Pacific Environmental Services (PES). Process conditions were monitored by Research Triangle Institute (RTI) during the field test.

## 3.2 FIELD TEST PROBLEMS AND CHANGES

Initially, the FTIR instrument was not working properly because the interferometer could not consistently hold alignment. An Analect service technician was consulted on 10/15. The technician suggested a slower scan speed and that helped the instrument function adequately, but a site visit was scheduled for 10/17. About one hour into Run 1 on 10/16 the instrument lost alignment. The alignment could not be recovered so FTIR testing was stopped. On 10/17 the Analect technician visited the site, repaired and realigned the interferometer. FTIR testing was resumed on 10/18 to coincide with Run 3 of the manual and M25A testing.

During the first test run, sample flow from the inlet location decreased rapidly to where it was only about 2 lpm when the FTIR testing was stopped after about one hour. The moisture combined with a high particulate level quickly clogged the particulate filter. Particulate did not clog the 50-ft section of heated line upstream of the filter. The flow problem was remedied by replacing the 3/8-in diameter sample probe with a ½-in. probe. When sampling was resumed for Run 3, the flow was higher and much more consistent for the run duration. Sample flow was much better at the scrubber outlet, but that probe was also replaced with a ½-in diameter probe.

TABLE 3-1. SCHEDULE OF FTIR TESTING AT EASTERN RIDGE

| Date | Time (Bkg & Cals) | Time (Sampling) | Kiln No 2. Scrubber Inlet | Kiln No 2. Scrubber Outlet | Hydrator |
|---|---|---|---|---|---|
| | | | | | |
| 10/15/96 | 1700-1758 | | Calibration and leak check | | |
| 10/16/96 | 907-1318 | | Background and Calibrations | | |
| | | 1455-1550 | Inlet to scrubber | | |
| 10/17/96 | 1835-2000 | | Background after cell alignment | | |
| 10/18/96 | 947-1042 | | Background, calibration, and leak check | | |
| | | 1044-1117 | Unspiked | Unspiked | |
| | | 1122-1139 | SF6 spike | Unspiked | |
| | | 1144-1236 | HCl spike | Unspiked | |
| | | 1237 | Spike off to inlet | | |
| | | 1244-1325 | Unspiked | Unspiked | |
| | 1345 | | Background | | |
| | | 1355-1612 | Unspiked | Unspiked | |
| | 1627 | | Background | | |
| | 1633 | | Calibration | | |
| 10/19/96 | 932-1145 | | | | Background and calibrations at hydrator stack |
| | | 1206-1244 | | | Hydrator stack |
| | 1240 | | | | Background |
| | | 1247-1314 | | | Hydrator stack hot wet |
| | 1342-1406 | | | | Calibration |
| | | 1409 | | | Started SF6 spike to probe |
| | 1410 | | | | Calibration |
| | | 1419-1434 | | | Hot wet spiked w/SF6 |
| | | 1436 | | | started HCl spike |
| | | 1444-1531 | | | spiked w/ HCl |
| | 1609-1620 | | | | Background and calibration |

## 3.3 SCRUBBER INLET

On October 16 limited testing was completed for about one hour before the FTIR instrument malfunction occurred. A full test run was completed on October 18. The principal emissions were water vapor, $CO_2$, $SO_2$, CO, and HCl. The HCl was not detected in samples that had been treated with the condenser system. The concentration results are presented in Table 3-2. Results for $SO_2$, CO, and HCl are presented graphically in Figures 3-1 to 3-3. Some HCl emissions were measured at the inlet and, in addition, three samples were spiked with the HCl gas standard to determine if sampling system introduced any bias in the measured HCl concentrations.

The estimated spike recovery is given in Table 3-2. Four samples spiked with HCl were collected (samples 208-211). It is apparent from Table 3-2 that the spiked HCl concentration was still increasing toward the expected value. Collecting additional samples may have given a higher percent recovery.

## 3.4 SCRUBBER OUTLET

Table 3-3 and Figures 3-4 to 3-7 present the results from the scrubber outlet. The west outlet stack (B) was sampled for the first part of the run. Then the probe was moved to the east (A) stack, which was tested for the remainder of the run.

The effluent at the outlet of both scrubber stacks was cooler and had a higher moisture content than at the inlet location. In addition, a wet scrubber is expected to provide an effective control for the emission of HCl, which is very soluble. The $SO_2$ emissions were significantly reduced compared to the inlet concentrations. The peak HCl emission at the outlet was almost 15 ppm, about half the peak HCl emission measured at the inlet.

## 3.5 HYDRATOR STACK

Moisture at the hydrator stack was about 60 percent. It was necessary to maintain flow through the manifold at at least about 5 LPM to prevent condensation in the rotameter. The HCl spike was observed but not recovered quantitatively.

TABLE 3-2. FTIR RESULTS FROM THE EASTRIDGE SCRUBBER INLET, 10/18/96.

| File name [1] | Time | $SO_2$ ppm | 4 * σ | $SO_2$ lbs/hr | $SF_6$ ppm | 4 * σ | CO ppm | 4 * σ | CO lbs/hr | HCl ppm | 4 * σ | HCl lbs/hr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SCINL001.SPC | 10/16/96 15:02 | | | | | | | | | 0.00 | 2.56 | 0.0 |
| SCINL002.SPC | 10/16/96 15:12 | | | | | | | | | 23.86 | 2.29 | 3.7 |
| SCINL201.SPC | 10:52 | 235.2 | 7.8 | 74.3 | 0.052 | 0.042 | 134.1 | 30.6 | 18.5 | 4.56 | 2.16 | 0.8 |
| SCINL202.SPC | 10:57 | 243.8 | 7.7 | 77.1 | 0.054 | 0.041 | 139.6 | 29.2 | 19.3 | 14.43 | 2.01 | 2.6 |
| SCINL203.SPC | 11:09 | 268.6 | 8.1 | 84.9 | 0.065 | 0.043 | 154.3 | 30.8 | 21.3 | 10.75 | 1.93 | 1.9 |
| SCINL204.SPC | 11:13 | 265.0 | 8.1 | 83.7 | 0.062 | 0.043 | 127.3 | 29.9 | 17.6 | 21.92 | 2.01 | 3.9 |
| SCINS205.SPC | 11:29 | 175.7 | 12.9 | 60.8 | **0.329** | **0.069** | 81.2 | 21.8 | 12.3 | 4.45 | 1.29 | 0.9 |
| SCINS206.SPC | 11:33 | 156.0 | 12.4 | 54.0 | **0.353** | **0.066** | 67.7 | 21.6 | 10.3 | 5.91 | 1.24 | 1.2 |
| SCINS207.SPC | 11:38 | 174.9 | 11.4 | 60.5 | **0.364** | **0.061** | 77.6 | 21.4 | 11.7 | 5.44 | 1.15 | 1.1 |
| SCINH208.SPC | 11:58 | 167.6 | 16.8 | 58.0 | 0.000 | 0.087 | 51.3 | 24.3 | 7.8 | **4.36** | **1.30** | |
| SCINH209.SPC | 12:08 | 202.8 | 14.8 | 70.2 | 0.000 | 0.078 | 62.5 | 21.7 | 9.5 | **18.53** | **1.53** | |
| SCINH210.SPC | 12:19 | 151.3 | 14.6 | 52.4 | 0.000 | 0.076 | 43.9 | 22.2 | 6.6 | **30.92** | **1.65** | |
| SCINH211.SPC | 12:30 | 184.5 | 11.3 | 63.8 | 0.000 | 0.059 | 41.8 | 21.0 | 6.3 | **19.11** | **1.41** | |
| SCINL212.SPC | 13:02 | 261.4 | 8.0 | 82.6 | 0.063 | 0.043 | 48.2 | 31.2 | 6.7 | 9.32 | 1.93 | 1.7 |
| SCINL213.SPC | 13:08 | 312.0 | 8.3 | 98.6 | 0.065 | 0.044 | 51.9 | 32.1 | 7.2 | 22.31 | 2.09 | 4.0 |
| SCINC214.SPC | 13:13 | 201.3 | 5.1 | 63.6 | 0.032 | 0.027 | 63.0 | 13.6 | 8.7 | 2.06 | 0.49 | 0.4 |
| SCINC215.SPC | 13:20 | 179.9 | 5.1 | 56.9 | 0.035 | 0.027 | 52.1 | 12.4 | 7.2 | 0.90 | 0.48 | 0.2 |
| SCINC216.SPC | 13:55 | 211.7 | 4.9 | 66.9 | 0.000 | 0.026 | 61.0 | 12.5 | 8.4 | 0.68 | 0.49 | 0.1 |
| SCINL217.SPC | 14:54 | 245.6 | 7.6 | 77.6 | 0.052 | 0.041 | 41.8 | 30.8 | 5.8 | 29.17 | 2.02 | 5.2 |
| SCIND218.SPC | 15:07 | 100.4 | 4.8 | 31.7 | 0.000 | 0.025 | 35.0 | 13.2 | 4.8 | 14.32 | 1.07 | 2.6 |
| SCINL219.SPC | 15:24 | 191.0 | 10.7 | 60.4 | 0.000 | 0.057 | 54.5 | 33.8 | 7.5 | 16.69 | 3.02 | 3.0 |
| SCINC220.SPC | 15:30 | 168.2 | 9.0 | 53.2 | 0.000 | 0.048 | 60.4 | 13.5 | 8.3 | 1.37 | 0.54 | 0.2 |
| SCIND221.SPC | 15:48 | 106.8 | 4.9 | 33.7 | 0.000 | 0.026 | 25.8 | 15.7 | 3.6 | 6.29 | 0.80 | 1.1 |
| SCINL222.SPC | 15:55 | 204.9 | 7.5 | 64.7 | 0.042 | 0.040 | 37.2 | 31.6 | 5.1 | 7.61 | 1.62 | 1.4 |
| average lbs/hour | | | | 59.6 | | | | | 8.9 | | | 1.8 |

| | | | | | |
|---|---|---|---|---|---|
| $SF_6$ standard = | 4.01 | HCl spike-unspike = | 12.03 | average HCl spike = 22.85 | |
| average $SF_6$ = | 0.349 | HCl "expected" = | 8.97 | average HCl unspike = 10.83 | |
| dilution = 4.01/.349 | 11.5 | percent deviation - spike from unspike = | | 25.45% | |

| | |
|---|---|
| DSCFM = | 29031 |
| % moisture = | 8.37 |

1 - File name: "SCINL" untreated scrubber inlet sample; "F" flowing; bold, in box, spiked ("S" with SF6, samples 208 to 211 spiked with HCl); "D" - dilution sample; "C" condenser sample.
"4"sigma" - estimated uncertainty.

TABLE 3-2. (continued)

| File name [1] | Date | Time | NO ppm | 4 * σ | NO lbs/hr | Time | NO2 ppm | 4 * σ | NO2 lbs/hr |
|---|---|---|---|---|---|---|---|---|---|
| SCINL001.SPC | 10/16/96 | 15:02:00 | 661.1 | 363.3 | 84.0 | 15:02:00 | 0 | 48.7 | |
| SCINL002.SPC | 10/16/96 | 15:12:00 | 620.5 | 315.3 | 78.8 | 15:12:00 | 0 | 47.4 | |
| SCINL201.SPC | 10/18/96 | 10:52:00 | 592.9 | 272.3 | 87.8 | 10:52:00 | 0 | 236.3 | |
| SCINL202.SPC | 10/18/96 | 10:57:00 | 585.3 | 249.3 | 86.7 | 10:57:00 | 0 | 189.6 | |
| SCINL203.SPC | 10/18/96 | 11:09:00 | 565.4 | 244.7 | 83.7 | 11:09:00 | 0 | 182.2 | |
| SCINL204.SPC | 10/18/96 | 11:13:00 | 577.5 | 250.1 | 85.5 | 11:13:00 | 0 | 190.9 | |
| SCINS205.SPC | 10/18/96 | 11:29:00 | 387.9 | 139.1 | 57.5 | 11:29:00 | 0 | 33.7 | |
| SCINS206.SPC | 10/18/96 | 11:33:00 | 398.0 | 138.9 | 58.9 | 11:33:00 | 0 | 25.5 | |
| SCINS207.SPC | 10/18/96 | 11:38:00 | 379.1 | 131.6 | 56.2 | 11:38:00 | 0 | 22.5 | |
| SCINH208.SPC | 10/18/96 | 11:58:00 | 378.7 | 151.7 | 56.1 | 11:58:00 | 0 | 131.6 | |
| SCINH209.SPC | 10/18/96 | 12:08:00 | 388.5 | 150.9 | 57.6 | 12:08:00 | 0 | 104.5 | |
| SCINH210.SPC | 10/18/96 | 12:19:00 | 406.0 | 149.3 | 60.1 | 12:19:00 | 0 | 37.1 | |
| SCINH211.SPC | 10/18/96 | 12:30:00 | 388.6 | 140.2 | 57.6 | 12:30:00 | 0 | 29.0 | |
| SCINL212.SPC | 10/18/96 | 13:02:00 | 572.7 | 247.6 | 84.8 | 13:02:00 | 0 | 187.3 | |
| SCINL213.SPC | 10/18/96 | 13:08:00 | 557.0 | 246.8 | 82.5 | 13:08:00 | 0 | 191.7 | |
| SCINC214.SPC | 10/18/96 | 13:13:00 | 417.1 | 85.9 | 61.8 | 13:13:00 | 13.0 | 8.8 | 3.0 |
| SCINC215.SPC | 10/18/96 | 13:20:00 | 458.2 | 95.7 | 67.9 | 13:20:00 | 14.5 | 8.3 | 3.3 |
| SCINC216.SPC | 10/18/96 | 13:55:00 | 448.1 | 94.5 | 66.4 | 13:55:00 | 16.2 | 7.6 | 3.7 |
| SCINL217.SPC | 10/18/96 | 14:54:00 | 570.1 | 230.7 | 84.5 | 14:54:00 | 0 | 145.2 | |
| SCIND218.SPC | 10/18/96 | 15:07:00 | 353.4 | 74.2 | 52.3 | 15:07:00 | 0 | 9.5 | |
| SCINL219.SPC | 10/18/96 | 15:24:00 | 587.8 | 266.3 | 87.1 | 15:24:00 | 0 | 180.9 | |
| SCINC220.SPC | 10/18/96 | 15:30:00 | 459.7 | 102.4 | 68.1 | 15:30:00 | 14.3 | 8.6 | 3.2 |
| SCIND221.SPC | 10/18/96 | 15:48:00 | 359.5 | 91.2 | 53.2 | 15:48:00 | 0 | 12.2 | |
| SCINL222.SPC | 10/18/96 | 15:55:00 | 583.6 | 228.5 | 86.4 | 15:55:00 | 0 | 135.0 | |

1 - File name: "SCINL" untreated scrubber inlet sample; "F" flowing; "S" spiked (bold indicates $SF_6$ or HCl); "D" - dilution sample; "C" condenser sample.
"4*sigma" - estimated uncertainty.
Interference from moisture limits the NO2 analysis.

TABLE 3-3. FTIR RESULTS FROM THE EASTRIDGE SCRUBBER OUTLET, 10/18/96.

| File name [1] | | Time | $SO_2$ ppm | 4 * σ | $SO_2$ lbs/hr | CO ppm | 4 * σ | CO lbs/hr | HCl ppm | 4 * σ | HCl lbs/hr |
|---|---|---|---|---|---|---|---|---|---|---|---|
| SCOUT001.SPC | West Stack (B) | 10/16/96 15:25 | | | | | | | 0 | 1.72 | 0.0 |
| SCOUT002.SPC | | 10/16/96 15:48 | | | | | | | 0 | 1.55 | 0.00 |
| SCOUT201.SPC | | 10:44 | 31.0 | 9.1 | 5.1 | 92.2 | 31.2 | 6.6 | 14.47 | 3.26 | 1.35 |
| SCOUT202.SPC | | 10:47 | 14.8 | 9.8 | 2.4 | 111.0 | 32.3 | 8.0 | 5.23 | 3.42 | 0.49 |
| SCOUT203.SPC | | 11:02 | 0.0 | 9.5 | 0.0 | 91.0 | 33.4 | 6.5 | 4.70 | 3.22 | 0.44 |
| SCOUT204.SPC | | 11:05 | 0.0 | 9.9 | 0.0 | 106.4 | 33.4 | 7.6 | 0.00 | 3.18 | 0.00 |
| SCOUT205.SPC | | 11:18 | 13.7 | 9.7 | 2.3 | 115.4 | 32.8 | 8.3 | 5.81 | 3.14 | 0.54 |
| SCOUT206.SPC | | 11:23 | 15.4 | 9.8 | 2.5 | 94.8 | 33.5 | 6.8 | 3.28 | 3.12 | 0.31 |
| SCOUC207.SPC | | 11:47 | 5.4 | 4.1 | 0.9 | 62.6 | 12.0 | 4.5 | 0.79 | 0.48 | |
| SCOUC208.SPC | | 11:53 | 12.4 | 4.1 | 2.0 | 69.9 | 12.5 | 5.0 | 0.77 | 0.49 | |
| SCOUC209.SPC | | 12:37 | 12.8 | 4.3 | 2.1 | 50.7 | 11.6 | 3.6 | 2.50 | 0.53 | |
| SCOUT210.SPC | | 12:44 | 22.1 | 10.1 | 3.6 | 105.3 | 34.2 | 7.5 | 7.60 | 3.31 | 0.71 |
| SCOUD211.SPC | | 12:51 | 0.0 | 6.9 | 0.0 | 0.0 | 33.5 | 0.0 | 7.10 | 2.10 | 0.66 |
| SCOUD212.SPC | | 12:57 | 0.0 | 7.1 | 0.0 | 0.0 | 33.7 | 0.0 | 5.37 | 2.30 | 0.50 |
| SCOUT213.SPC | | 13:30 | 0.0 | 9.5 | 0.0 | 53.1 | 39.3 | 3.8 | 4.38 | 3.37 | 0.41 |
| Average lbs/hour = | | | | | 1.6 | | | 5.3 | | | 0.5 |
| SCOUT214.SPC | East Stack (A) | 14:06 | 0.0 | 7.4 | 0.0 | 49.6 | 32.4 | 4.9 | 2.11 | 2.00 | 0.27 |
| SCOUC215.SPC | | 14:13 | 30.8 | 4.4 | 7.0 | 73.8 | 13.7 | 7.3 | 0.00 | 0.56 | |
| SCOUC216.SPC | | 14:19 | 13.9 | 4.4 | 3.2 | 53.4 | 11.8 | 5.3 | 0.00 | 0.55 | |
| SCOUT217.SPC | | 14:28 | 0.0 | 7.7 | 0.0 | 47.7 | 33.9 | 4.7 | 0.00 | 2.16 | 0.00 |
| SCOUT218.SPC | | 14:41 | 0.0 | 10.6 | 0.0 | 0.0 | 47.5 | 0.0 | 0.00 | 3.48 | 0.00 |
| SCOUC219.SPC | | 14:46 | 5.9 | 4.5 | 1.3 | 45.7 | 12.4 | 4.5 | 0.00 | 0.56 | |
| SCOUC220.SPC | | 14:50 | 4.5 | 4.4 | 1.0 | 46.2 | 11.6 | 4.6 | 0.00 | 0.53 | |
| SCOUD221.SPC | | 15:00 | 0.0 | 5.9 | 0.0 | 0.0 | 26.4 | 0.0 | 10.46 | 1.48 | 1.35 |
| SCOUD222.SPC | | 15:03 | 0.0 | 3.4 | 0.0 | 0.0 | 13.0 | 0.0 | 9.11 | 0.70 | 1.18 |
| SCOUD223.SPC | | 15:15 | 0.0 | 5.8 | 0.0 | 0.0 | 26.2 | 0.0 | 8.71 | 1.45 | 1.12 |
| SCOUC224.SPC | | 15:20 | 0.0 | 4.4 | 0.0 | 51.4 | 12.1 | 5.1 | 0.77 | 0.53 | |
| SCOUC225.SPC | | 15:35 | 14.5 | 4.2 | 3.3 | 47.7 | 11.2 | 4.7 | 0.65 | 0.56 | |
| SCOUT226.SPC | | 15:42 | 0.0 | 9.0 | 0.0 | 0.0 | 43.5 | 0.0 | 4.41 | 2.72 | 0.57 |
| SCOUD227.SPC | | 16:00 | 0.0 | 2.2 | 0.0 | 0.0 | 9.8 | 0.0 | 10.78 | 0.56 | 1.39 |
| SCOUC228.SPC | | 16:05 | 7.8 | 4.2 | 1.8 | 43.0 | 11.3 | 4.3 | 0.64 | 0.53 | |
| SCOUT229.SPC | | 16:10 | 0.0 | 7.8 | 0.0 | 0.0 | 37.9 | 0.0 | 3.20 | 2.13 | 0.41 |
| Average lbs/hour = | | | | | 1.10 | | | 2.84 | | | 0.70 |

| | |
|---|---|
| A - DCFM = | 18613 |
| A - % moisture = | 18.1 |

| | |
|---|---|
| B - DSCFM = | 13633 |
| B - % moistu | 17 |

1 - File name: "SCOUT" scrubber outlet sample, untreated; "F" flowing; "D" - dilution sample; "C" condenser sample.
"4"sigma" - estimated uncertainty.

TABLE 3-3. (continued)

| File name [1] | | date | Time | NO ppm | 4 * σ | NO lbs/hr | NO2 ppm | 4 * σ | NO2 lbs/hr |
|---|---|---|---|---|---|---|---|---|---|
| SCOUT001.SPC | West Stack (B) | 10/16/96 | 15:25 | 537.5 | 404.7 | 35.6 | 0.0 | 18.7 | |
| SCOUT002.SPC | | 10/16/96 | 15:48 | 511.3 | 372.3 | 33.8 | 0.0 | 28.8 | |
| SCOUT201.SPC | | 10/18/96 | 10:44 | 549.5 | 371.2 | 42.2 | 0.0 | 365.4 | |
| SCOUT202.SPC | | 10/18/96 | 10:47 | 536.1 | 392.1 | 41.2 | 0.0 | 315.2 | |
| SCOUT203.SPC | | 10/18/96 | 11:02 | 536.2 | 373.0 | 41.2 | 0.0 | 339.5 | |
| SCOUT204.SPC | | 10/18/96 | 11:05 | 530.6 | 372.9 | 40.7 | 0.0 | 362.8 | |
| SCOUT205.SPC | | 10/18/96 | 11:18 | 521.8 | 369.9 | 40.1 | 0.0 | 356.4 | |
| SCOUT206.SPC | | 10/18/96 | 11:23 | 510.7 | 360.6 | 39.2 | 0.0 | 355.7 | |
| SCOUC207.SPC | | 10/18/96 | 11:47 | 319.4 | 60.3 | 24.5 | 14.0 | 8.0 | 1.6 |
| SCOUC208.SPC | | 10/18/96 | 11:53 | 313.9 | 57.5 | 24.1 | 9.9 | 7.7 | 1.2 |
| SCOUC209.SPC | | 10/18/96 | 12:37 | 334.2 | 62.8 | 25.7 | 13.6 | 8.5 | 1.6 |
| SCOUT210.SPC | | 10/18/96 | 12:44 | 507.5 | 377.6 | 39.0 | 0.0 | 341.4 | |
| SCOUD211.SPC | | 10/18/96 | 12:51 | 313.8 | 204.6 | 24.1 | 0.0 | 197.3 | |
| SCOUD212.SPC | | 10/18/96 | 12:57 | 326.5 | 210.1 | 25.1 | 0.0 | 198.3 | |
| SCOUT213.SPC | | 10/18/96 | 13:30 | 491.4 | 356.1 | 37.7 | 0.0 | 351.3 | |
| SCOUT214.SPC | | 10/18/96 | 14:06 | 479.2 | 248.6 | 36.8 | 0.0 | 239.8 | |
| SCOUC215.SPC | | 10/18/96 | 14:13 | 374.9 | 72.8 | 28.8 | 13.3 | 8.8 | 1.6 |
| Average lbs/hour = | | | | | | 34.0 | | | 1.5 |
| SCOUC216.SPC | East Stack (A) | 10/18/96 | 14:19 | 377.8 | 80.8 | 40.1 | 15.3 | 7.6 | 2.5 |
| SCOUT217.SPC | | 10/18/96 | 14:28 | 482.8 | 268.2 | 51.3 | 0.0 | 290.0 | |
| SCOUT218.SPC | | 10/18/96 | 14:41 | 524.2 | 390.4 | 55.7 | 0.0 | 284.5 | |
| SCOUC219.SPC | | 10/18/96 | 14:46 | 401.2 | 81.7 | 42.6 | 14.6 | 9.1 | 2.4 |
| SCOUC220.SPC | | 10/18/96 | 14:50 | 400.9 | 81.0 | 42.6 | 14.3 | 8.3 | 2.3 |
| SCOUD221.SPC | | 10/18/96 | 15:00 | 311.2 | 153.0 | 33.1 | 0.0 | 133.2 | |
| SCOUD222.SPC | | 10/18/96 | 15:03 | 132.3 | 62.8 | 14.1 | 0.0 | 9.8 | |
| SCOUD223.SPC | | 10/18/96 | 15:15 | 311.4 | 152.8 | 33.1 | 0.0 | 131.2 | |
| SCOUC224.SPC | | 10/18/96 | 15:20 | 404.9 | 82.3 | 43.0 | 14.3 | 8.6 | 2.3 |
| SCOUC225.SPC | | 10/18/96 | 15:35 | 391.3 | 83.6 | 41.6 | 14.4 | 7.8 | 2.3 |
| SCOUT226.SPC | | 10/18/96 | 15:42 | 515.4 | 331.2 | 54.8 | 0.0 | 359.2 | |
| SCOUD227.SPC | | 10/18/96 | 16:00 | 69.8 | 40.9 | 7.4 | 0.0 | 7.6 | |
| SCOUC228.SPC | | 10/18/96 | 16:05 | 384.0 | 84.9 | 40.8 | 17.8 | 8.4 | 2.9 |
| SCOUT229.SPC | | 10/18/96 | 16:10 | 533.7 | 281.9 | 56.7 | 0.0 | 271.8 | |
| Average lbs/hour = | | | | | | 39.77 | | | 2.46 |

1 - File name: "SCOUT" scrubber outlet sample, untreated; "F" flowing; "D" - dilution sample; "C" condenser sample.
"4*sigma" - estimated uncertainty.

TABLE 3-4. ESTIMATED HAP UNCERTAINTIES, EASTERN RIDGE SCRUBBER INLET AND OUTLET

| Compound | Analytical Region ($cm^{-1}$) | Scrubber Inlet RMSD | Scrubber Inlet Estimated Uncertainty (ppm) | Scrubber Outlet RMSD | Scrubber Outlet Estimated Uncertainty (ppm) |
|---|---|---|---|---|---|
| Acetonitrile | 3038.97 - 3042.42 | 1.1E-03 | 13.2 | 9.53E-03 | 98.63 |
| Acrolein | 2636.11 - 2875.59 | 1.9E-03 | 2.8 | 7.83E-03 | 11.35 |
| Acrylonitrile | 968.58 - 974.19 | 7.7E-03 | 4.1 | 2.01E-02 | 10.61 |
| Allyl Chloride | 899.55 - 965.72 | 1.1E-02 | 7.5 | 4.49E-02 | 31.55 |
| Benzene | 3036.88 - 3063.07 | 2.7E-02 | 14.0 | 2.16E-01 | 112.30 |
| Bromoform | 1135.9 - 1154.2 | 9.0E-03 | 1.9 | 1.20E-01 | 24.99 |
| 1,3-Butadiene | 895.91 - 919.75 | 3.8E-03 | 1.3 | 5.45E-02 | 18.20 |
| Carbonyl Sulfide | 2026.14 - 2085.23 | 3.6E-01 | 12.8 | 4.84E-01 | 17.48 |
| Chlorobenzene | 1069.86 - 1103.34 | 8.0E-03 | 4.3 | 5.70E-02 | 30.89 |
| Ethyl Benzene | 2850.71 - 2959.43 | 7.5E-03 | 10.2 | 6.56E-02 | 88.68 |
| Ethyl Chloride | 943.43 - 1000.16 | 1.0E-02 | 16.1 | 2.64E-02 | 40.86 |
| Ethylene Dibromide | 1167.96 - 1208.92 | 1.3E-02 | 10.5 | 1.89E-01 | 149.17 |
| n-Hexane | 2835.27 - 3005.43 | 1.2E-02 | 2.0 | 1.15E-01 | 18.54 |
| Methyl Bromide | 2948.11 - 2972.53 | 1.4E-02 | 17.4 | 1.05E-01 | 133.50 |
| Methyl Chloride | 1017.96 - 1020.72 | 3.3E-03 | 12.0 | 1.87E-02 | 67.99 |
| Methyl Ethyl Ketone | 1140.7 - 1222.63 | 1.3E-02 | 10.9 | 1.83E-01 | 149.64 |
| Methyl Isobutyl Ketone | 2872.05 - 2994.95 | 1.3E-02 | 5.9 | 1.09E-01 | 51.10 |
| Methyl Methacrylate | 1137.5 - 1232.04 | 1.5E-02 | 1.9 | 3.71E-02 | 20.82 |
| Methylene Chloride | 743.96 - 769.17 | 1.4E-01 | 15.0 | 2.75E-01 | 29.46 |
| 2-Nitropropane | 831.47 - 868.5 | 7.0E-03 | 8.5 | 1.19E-01 | 145.47 |
| Propylene Dichloride | 996.86 - 1038 | 8.1E-03 | 10.6 | 4.00E-02 | 52.21 |
| Styrene | 886.69 - 920.72 | 3.5E-03 | 2.8 | 1.56E-02 | 21.72 |
| Tetrachloroethylene | 899.2 - 925.2 | 4.5E-03 | 0.5 | 5.88E-02 | 5.91 |
| Toluene | 2862 - 2924 | 4.1E-03 | 7.2 | 2.62E-02 | 45.90 |
| 1,1,2-Trichloroethane | 916.98 - 956.37 | 1.2E-02 | 9.1 | 3.71E-02 | 28.96 |
| Trichloroethylene | 826.25 - 860.91 | 7.6E-03 | 1.3 | 3.87E-02 | 8.24 |
| 2,2,4-Trimethylpentane | 2861.57 - 3009.23 | 1.3E-02 | 1.8 | 1.23E-01 | 16.45 |
| Vinyl Acetate | 1201.77 - 1242.73 | 1.8E-02 | 0.8 | 1.06E-01 | 10.42 |
| Vinyl Bromide | 899.81 - 904.54 | 1.7E-03 | 0.8 | 1.35E-03 | 0.63 |
| Vinyl Chloride | 894.43 - 899.25 | 1.1E-03 | 2.0 | 9.69E-03 | 18.29 |
| Vinylidene Chloride | 1059.44 - 1113.01 | 1.1E-02 | 3.2 | 7.45E-02 | 22.02 |
| O-xylene | 2859.84 - 3095.04 | 2.4E-02 | 16.8 | 2.05E-01 | 144.20 |
| P-xylene | 2854.43 - 3083.14 | 2.3E-02 | 14.1 | 2.01E-01 | 121.88 |



See Section 4.8, Screening For HAPs.

TABLE 3-4. CONTINUED

| Compound | Analytical Region ($cm^{-1}$) | Scrubber Inlet RMSD | Scrubber Inlet Estimated Uncertainty (ppm) | Scrubber Outlet RMSD | Scrubber Outlet Estimated Uncertainty (ppm) |
|---|---|---|---|---|---|
| Carbon Disulfide | 2171.64 - 2198.03 | 7.8E-03 | 8.5 | 5.19E-02 | 56.16 |
| Carbon Tetrachloride | 793.89 - 800.58 | 3.5E-02 | 0.8 | 2.17E-01 | 4.68 |
| Chloroform | 758.21 - 781.25 | 5.4E-02 | 3.0 | 1.17E-01 | 6.56 |
| Cumene | 2951.21 - 2998.48 | 1.8E-02 | 5.2 | 1.60E-01 | 45.11 |
| 1,2-Epoxy Butane | 902.37 - 919.7 | 4.4E-03 | 3.5 | 5.85E-02 | 47.22 |
| Ethylene Oxide | 866.9 - 875 | 3.9E-03 | 1.0 | 2.75E-02 | 7.33 |
| Methanol | 2807.91 - 3029.4 | 1.5E-02 | 13.5 | 1.34E-01 | 119.19 |
| Methyl Chloroform | 1057.95 - 1105.3 | 1.1E-02 | 2.2 | 6.71E-02 | 13.06 |
| Methyl Iodide | 1250.18 - 1253.53 | 1.5E-03 | 1.5 | 8.99E-03 | 9.02 |
| Methyl t-Butyl Ether | 1195 - 1210 | 8.0E-03 | 1.4 | 6.71E-02 | 12.53 |
| Propylene Oxide | 2875.59 - 3097.75 | 2.5E-02 | 17.8 | 2.15E-01 | 150.95 |
| M-xylene | 2910.25 - 2952.78 | 8.8E-03 | 5.9 | 7.87E-02 | 53.09 |
| Acetone | 1182 - 1255.03 | 1.7E-02 | 8.1 | 2.52E-01 | 121.27 |
| Acetaldehyde | 2685.41 - 2744.4 | 1.5E-03 | 2.8 | 9.53E-03 | 17.35 |
| Acetophenone | 1140.4 - 1286.06 | 3.0E-02 | 4.3 | 3.41E-01 | 48.76 |
| Acrylic Acid | 1104.89 - 1164.68 | 8.5E-03 | 1.2 | 9.74E-02 | 13.53 |
| Aniline | 1102.9 - 1123.63 | 8.1E-03 | 2.9 | 9.00E-02 | 31.73 |
| Benzotrichloride | 866.5 - 877.9 | 3.7E-03 | 0.7 | 2.47E-02 | 5.00 |
| Benzyl Chloride | 3027.52 - 3109.06 | 3.7E-02 | 32.1 | 3.06E-01 | 264.80 |
| Bis(chloromethyl)ether | 1068.78 - 1154.25 | 1.0E-02 | 1.2 | 8.76E-02 | 10.34 |
| Chloroacetic acid | 1094.97 - 1124.12 | 7.2E-03 | 1.7 | 8.28E-02 | 19.48 |
| 2-Chloroacteophenone | 1274.39 - 1285.42 | 1.2E-02 | 2.5 | 2.61E-01 | 53.08 |
| Chloromethyl methyl ether | 1111.02 - 1146.08 | 9.4E-03 | 1.5 | 1.04E-01 | 16.70 |
| Chloroprene | 875.9 - 878.8 | 3.6E-03 | 0.7 | 1.94E-02 | 3.83 |
| o-Cresol | 1092.8 - 1114.07 | 5.9E-03 | 2.7 | 7.34E-02 | 33.83 |
| m-Cresol | 1139.68 - 1172.77 | 6.5E-03 | 1.3 | 7.20E-02 | 14.25 |
| p-Cresol | 1159.1 - 1185.5 | 1.2E-02 | 1.4 | 1.89E-01 | 22.79 |
| 1,2-Dibromo-3-chloropropane | 1134.26 - 1175.42 | 1.2E-02 | 15.0 | 1.76E-01 | 218.20 |
| 1,4-Dichlorobenzene | 995.96 - 1031.06 | 4.3E-03 | 2.0 | 4.03E-02 | 19.20 |
| Dichloroethyl ether | 1109.35 - 1155.04 | 8.9E-03 | 1.1 | 1.01E-01 | 12.54 |
| 1,3-Dichloropropene | 768 - 791 | 3.9E-02 | 8.6 | 1.40E-01 | 31.04 |
| Dichlorvos | 835.77 - 876.95 | 6.8E-03 | 0.9 | 1.88E-02 | 2.90 |
| N,N-Diethyl aniline | 2655.32 - 3156.07 | 2.3E-02 | 14.2 | 1.89E-01 | 119.51 |
| Dimethyl carbamoyl chloride | 889.55 - 917.52 | 3.3E-03 | 0.9 | 6.53E-02 | 10.03 |



See Section 4.8, Screening For HAPs.

TABLE 3-4. CONTINUED

| Compound | Analytical Region ($cm^{-1}$) | Scrubber Inlet RMSD | Scrubber Inlet Estimated Uncertainty (ppm) | Scrubber Outlet RMSD | Scrubber Outlet Estimated Uncertainty (ppm) |
|---|---|---|---|---|---|
| Dimethyl formamide | 2824.8 - 2873.6 | 2.0E-03 | 1.4 | 8.70E-03 | 5.98 |
| 1,1-Dimethyl hydrazine | 2740.77 - 2914.08 | 3.1E-03 | 1.5 | 1.62E-02 | 8.13 |
| Dimethyl phthalate | 1157.86 - 1254.16 | 1.6E-02 | 9.3 | 2.41E-01 | 138.37 |
| 1,4-Dioxane | 2919.4 - 2921.3 | 8.9E-04 | 0.2 | 8.98E-04 | 0.30 |
| Epichlorohydrin | 943.52 - 981.73 | 1.2E-02 | 10.8 | 3.06E-02 | 27.18 |
| Ethyl Acrylate | 1181.93 - 1210 | 1.2E-02 | 0.7 | 1.46E-01 | 8.08 |
| Ethylene Dichloride | 1227.88 - 1241.5 | 6.4E-03 | 3.9 | 9.00E-02 | 54.79 |
| Ethylidene dichloride | 1041.11 - 1080.5 | 1.5E-02 | 6.9 | 5.86E-02 | 27.19 |
| Formaldehyde | 2788.33 - 2842.2 | 1.7E-03 | 1.9 | 6.73E-03 | 7.35 |
| Hexachlorobutadiene | 976.9 - 997.7 | 5.3E-03 | 0.8 | 8.21E-03 | 1.25 |
| Hexachlorocylcopentadiene | 1227.02 - 1240.42 | 6.4E-03 | 0.5 | 9.26E-02 | 7.61 |
| Hexachloroethane | 779.26 - 797.38 | 9.0E-01 | 20.7 | 1.03E+00 | 23.76 |
| Hexamethylphosphoramide | 949.42 - 1019.53 | 8.5E-03 | 1.3 | 3.32E-02 | 4.92 |
| Maleic Anhydride | 2817.35 - 2823.26 | 1.9E-03 | 2.1 | 6.87E-03 | 7.30 |
| Methyl hydrazine | 2681.2 - 3130.6 | 2.3E-02 | 15.6 | 1.86E-01 | 128.28 |
| Naphthalene | 885.27 - 905.56 | 1.8E-03 | 0.2 | 2.55E-02 | 2.76 |
| Nitrobenzene | 2683 - 3061.78 | 1.6E-02 | 19.0 | 1.48E-01 | 176.38 |
| N-Nitrosodimethylene | 779.31 - 783.55 | 1.5E-02 | 1.6 | 5.60E-02 | 5.95 |
| N-Nitrosomorpholine | 841.7 - 861.39 | 8.2E-03 | 3.5 | 1.40E-01 | 60.04 |
| Phenol | 928 - 1085.28 | 1.2E-02 | 4.0 | 4.15E-02 | 13.97 |
| beta-Propiolactone | 892.23 - 1024.64 | 9.3E-03 | 4.0 | 4.18E-02 | 18.18 |
| Propionaldehyde | 998.4 - 999.9 | 1.7E-04 | 0.9 | 8.16E-03 | 17.59 |
| 1,2-Propylenimine | 860.13 - 957.64 | 8.8E-03 | 2.0 | 4.76E-02 | 10.79 |
| Quioline | 2546.18 - 3114.35 | 1.8E-02 | 20.9 | 1.58E-01 | 184.09 |
| Styrene Oxide | 817.57 - 821.31 | 4.3E-03 | 2.0 | 3.97E-03 | 1.86 |
| 1,1,2,2-Tetrachloroethane | 800.19 - 803.73 | 2.0E-02 | 3.3 | 1.31E-01 | 21.21 |
| 2,4-Toluene diisocyanate | 861.39 - 903.93 | 3.2E-03 | 2.5 | 4.49E-02 | 34.30 |
| o_Tolnidine | 794.92 - 824.07 | 1.8E-02 | 4.4 | 1.57E-01 | 38.75 |
| 1,2,4-Trichlorobenzene | 2254.7 - 2301.18 | 5.3E-02 | 0.9 | 7.94E-02 | 1.30 |
| 2,4,5-Trichlorophenol | 2858.5 - 2951.85 | 6.7E-03 | 6.1 | 6.37E-03 | 25.45 |
| 2,4,6-Trichlorophenol | 1086.21 - 1114.37 | 6.5E-03 | 1.8 | 2.72E-02 | 9.38 |
| Triethylamine | 1178.04 - 1204.16 | 1.2E-02 | 4.1 | 1.53E-01 | 50.79 |
| Ammonia | 856.27 - 863.36 | 2.5E-03 | 0.6 | 4.05E-02 | 10.47 |
| Ammonia | 2756.62 - 2839.34 | 1.8E-03 | 0.8 | 6.16E-03 | 2.84 |



See Section 4.8, Screening For HAPs.

TABLE 3-5. EASTERN RIDGE HYDRATOR ESTIMATED HAP UNCERTAINTIES

| Compound | Hydrator Stack Analytical Region ($cm^{-1}$) | | | RMSD | Estimated Uncertainty (ppm) |
|---|---|---|---|---|---|
| Acetonitrile | 1041.4 | - | 1042.88 | 4.2E-03 | 23.9 |
| Acrolein | 2636.11 | - | 2875.59 | 3.5E-03 | 5.1 |
| Acrylonitrile | 968.58 | - | 974.19 | 6.7E-03 | 3.6 |
| Allyl Chloride | 899.55 | - | 965.72 | 2.1E-02 | 14.5 |
| Benzene | 3036.88 | - | 3063.07 | 1.5E-01 | 78.3 |
| Bromoform | 1135.9 | - | 1154.2 | 7.3E-02 | 15.2 |
| 1,3-Butadiene | 895.91 | - | 919.75 | 2.7E-02 | 9.1 |
| Carbonyl Sulfide | 2026.14 | - | 2085.23 | 2.5E-01 | 8.9 |
| Chlorobenzene | 1069.86 | - | 1103.34 | 2.8E-02 | 15.4 |
| Ethyl Benzene | 2850.71 | - | 2959.43 | 3.2E-02 | 43.6 |
| Ethyl Chloride | 943.43 | - | 1000.16 | 1.0E-02 | 15.8 |
| Ethylene Dibromide | 1167.96 | - | 1208.92 | 1.3E-01 | 103.2 |
| n-Hexane | 2835.27 | - | 3005.43 | 6.6E-02 | 10.6 |
| Methyl Bromide | 2948.11 | - | 2972.53 | 5.4E-02 | 69.2 |
| Methyl Chloride | 1017.96 | - | 1020.72 | 8.3E-03 | 30.2 |
| Methyl Ethyl Ketone | 1140.7 | - | 1222.63 | 1.2E-01 | 100.6 |
| Methyl Isobutyl Ketone | 2872.05 | - | 2994.95 | 6.3E-02 | 29.3 |
| Methyl Methacrylate | 915.64 | - | 962.12 | 1.5E-02 | 8.5 |
| Methylene Chloride | 743.96 | - | 769.17 | 1.5E-01 | 15.8 |
| 2-Nitropropane | 831.47 | - | 868.5 | 6.7E-02 | 81.6 |
| Propylene Dichloride | 996.86 | - | 1038 | 1.7E-02 | 21.7 |
| Styrene | 974.29 | - | 1006.59 | 5.1E-03 | 7.1 |
| Tetrachloroethylene | 899.2 | - | 925.2 | 2.9E-02 | 2.9 |
| Toluene | 2862 | - | 2924 | 1.2E-02 | 20.3 |
| 1,1,2-Trichloroethane | 916.98 | - | 956.37 | 1.6E-02 | 12.3 |
| Trichloroethylene | 919.7 | - | 959.88 | 1.6E-02 | 3.4 |
| 2,2,4-Trimethylpentane | 2861.57 | - | 3009.23 | 7.0E-02 | 9.4 |
| Vinyl Acetate | 1003.83 | - | 1041.65 | 1.7E-02 | 5.3 |
| Vinyl Bromide | 899.81 | - | 904.54 | 1.4E-03 | 0.6 |
| Vinyl Chloride | 894.43 | - | 899.25 | 4.1E-03 | 7.7 |
| Vinylidene Chloride | 1059.44 | - | 1113.01 | 4.0E-02 | 11.8 |
| O-xylene | 2859.84 | - | 3095.04 | 1.3E-01 | 92.0 |



See Section 4.8, Screening For HAPs

TABLE 3-5. CONTINUED

| Compound | Hydrator Stack Analytical Region ($cm^{-1}$) | | | RMSD | Estimated Uncertainty (ppm) |
|---|---|---|---|---|---|
| P-xylene | 770.61 | - | 819.06 | 1.2E-01 | 76.5 |
| Carbon Disulfide | 2171.64 | - | 2198.03 | 3.1E-02 | 33.2 |
| Carbon Tetrachloride | 793.89 | - | 800.58 | 1.8E-01 | 4.0 |
| Chloroform | 758.21 | - | 781.25 | 6.6E-02 | 3.7 |
| Cumene | 1015.6 | - | 1040.81 | 1.1E-02 | 25.6 |
| 1,2-Epoxy Butane | 902.37 | - | 919.7 | 3.0E-02 | 24.0 |
| Ethylene Oxide | 866.9 | - | 875 | 1.4E-02 | 3.8 |
| Methanol | 2807.91 | - | 3029.4 | 8.0E-02 | 71.7 |
| Methyl Chloroform | 1057.95 | - | 1105.3 | 3.4E-02 | 6.6 |
| Methyl Iodide | 1250.18 | - | 1253.53 | 5.5E-03 | 5.5 |
| Methyl t-Butyl Ether | 1070.6 | - | 1109 | 3.7E-02 | 6.9 |
| Propylene Oxide | 2875.59 | - | 3097.75 | 1.4E-01 | 96.6 |
| M-xylene | 2910.25 | - | 2952.78 | 3.9E-02 | 26.4 |
| Acetone | 1182 | - | 1255.03 | 1.7E-01 | 81.5 |
| Acetaldehyde | 2685.41 | - | 2744.4 | 4.1E-03 | 7.5 |
| Acetophenone | 874.88 | - | 1126.36 | 2.7E-02 | 24.5 |
| Acrylic Acid | 953.62 | - | 1046.71 | 1.3E-02 | 6.5 |
| Aniline | 1102.9 | - | 1123.63 | 5.2E-02 | 18.2 |
| Benzotrichloride | 866.5 | - | 877.9 | 1.3E-02 | 2.6 |
| Benzyl Chloride | 3027.52 | - | 3109.06 | 2.0E-01 | 174.2 |
| Bis(chloromethyl)ether | 1068.78 | - | 1154.25 | 5.2E-02 | 6.1 |
| Chloroacetic acid | 1094.97 | - | 1124.12 | 4.6E-02 | 10.9 |
| 2-Chloroacteophenone | 1274.39 | - | 1285.42 | 1.7E-01 | 35.2 |
| Chloromethyl methyl ether | 1111.02 | - | 1146.08 | 6.5E-02 | 10.5 |
| Chloroprene | 875.9 | - | 878.8 | 1.1E-02 | 2.2 |
| o-Cresol | 1092.8 | - | 1114.07 | 4.2E-02 | 19.4 |
| m-Cresol | 1139.68 | - | 1172.77 | 3.8E-02 | 7.4 |
| p-Cresol | 2865.7 | - | 2893 | 5.6E-03 | 11.2 |
| 1,2-Dibromo-3-chloropropane | 1134.26 | - | 1175.42 | 1.1E-01 | 140.6 |
| 1,4-Dichlorobenzene | 995.96 | - | 1031.06 | 1.8E-02 | 8.4 |
| Dichloroethyl ether | 1109.35 | - | 1155.04 | 6.2E-02 | 7.7 |
| 1,3-Dichloropropene | 768 | - | 791 | 8.3E-02 | 18.4 |
| Dichlorvos | 967.79 | - | 1000.25 | 6.3E-03 | 1.0 |



See Section 4.8, Screening For HAPs

TABLE 3-5. CONTINUED

| Compound | Hydrator Stack Analytical Region ($cm^{-1}$) | | | RMSD | Estimated Uncertainty (ppm) |
|---|---|---|---|---|---|
| N,N-Diethyl aniline | 2655.32 | - | 3156.07 | 1.2E-01 | 77.5 |
| Dimethyl carbamoyl chloride | 1068.78 | - | 1114.47 | 3.6E-02 | 5.5 |
| Dimethyl formamide | 2824.8 | - | 2873.6 | 3.5E-03 | 2.4 |
| 1,1-Dimethyl hydrazine | 2740.77 | - | 2914.08 | 7.4E-03 | 3.7 |
| Dimethyl phthalate | 1157.86 | - | 1254.16 | 1.6E-01 | 92.5 |
| 1,4-Dioxane | 2861.1 | - | 2864.8 | 2.5E-03 | 0.4 |
| Epichlorohydrin | 943.52 | - | 981.73 | 1.2E-02 | 10.7 |
| Ethyl Acrylate | 1181.93 | - | 1210 | 1.1E-01 | 5.9 |
| Ethylene Dichloride | 712 | - | 736 | 1.5E-01 | 30.0 |
| Ethylidene dichloride | 1041.11 | - | 1080.5 | 2.9E-02 | 13.5 |
| Formaldehyde | 2788.33 | - | 2842.2 | 3.6E-03 | 4.0 |
| Hexachlorobutadiene | 976.9 | - | 997.7 | 2.5E-03 | 0.4 |
| Hexachlorocylcopentadiene | 1227.02 | - | 1240.42 | 5.5E-02 | 4.5 |
| Hexachloroethane | 779.26 | - | 797.38 | 9.4E-02 | 2.2 |
| Hexamethylphosphoramide | 949.42 | - | 1019.53 | 1.4E-02 | 2.1 |
| Hydrochloric Acid | 2817.35 | - | 2823.26 | 3.5E-03 | 3.7 |
| Isophorone | 2681.2 | - | 3130.6 | 1.2E-01 | 83.4 |
| Maleic Anhydride | 885.27 | - | 905.56 | 1.1E-02 | 1.2 |
| Methyl hydrazine | 2683 | - | 3061.78 | 9.4E-02 | 111.9 |
| Naphthalene | 779.31 | - | 783.55 | 3.5E-02 | 3.8 |
| Nitrobenzene | 841.7 | - | 861.39 | 8.2E-02 | 35.3 |
| N-Nitrosodimethylene | 928 | - | 1085.28 | 1.9E-02 | 6.3 |
| N-Nitrosomorpholine | 892.23 | - | 1024.64 | 1.8E-02 | 7.8 |
| Phenol | 1024 | - | 1026.6 | 4.6E-04 | 2.3 |
| beta-Propiolactone | 860.13 | - | 957.64 | 2.1E-02 | 4.9 |
| Propionaldehyde | 2546.18 | - | 3114.35 | 1.0E-01 | 116.3 |
| 1,2-Propylenimine | 817.57 | - | 821.31 | 6.7E-04 | 0.3 |
| Quinoline | 800.19 | - | 803.73 | 9.0E-02 | 14.5 |
| Styrene Oxide | 861.39 | - | 903.93 | 2.0E-02 | 15.2 |
| 1,1,2,2-Tetrachloroethane | 794.92 | - | 824.07 | 1.1E-01 | 28.4 |
| 2,4-Toluene diisocyanate | 2254.7 | - | 2301.18 | 3.4E-02 | 0.6 |
| o_Toluidine | 979 | - | 997.8 | 1.8E-03 | 7.2 |
| 1,2,4-Trichlorobenzene | 1028.2 | - | 1048.69 | 8.9E-03 | 3.1 |



See Section 4.8, Screening For HAPs

TABLE 3-5. CONTINUED

| Compound | Hydrator Stack Analytical Region ($cm^{-1}$) | | | RMSD | Estimated Uncertainty (ppm) |
|---|---|---|---|---|---|
| 2,4,5-Trichlorophenol | 1178.04 | - | 1204.16 | 1.1E-01 | 37.4 |
| 2,4,6-Trichlorophenol | 856.27 | - | 863.36 | 1.9E-02 | 4.9 |
| Triethylamine | 2756.62 | - | 2839.34 | 3.2E-03 | 1.5 |
| Ammonia | 893.1 | - | 926 | 2.6E-02 | 17.2 |



See Section 4.8, Screening For HAPs

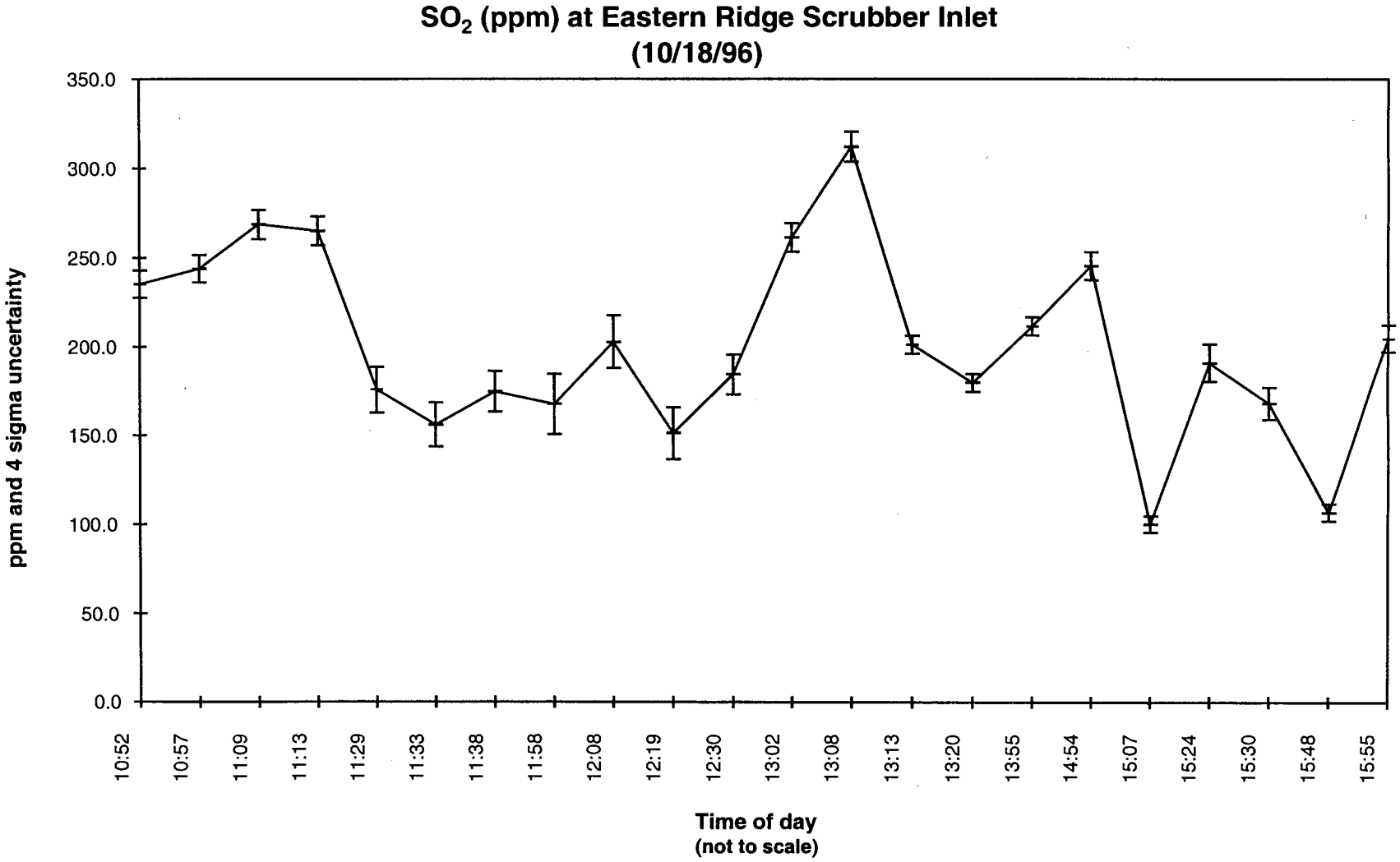



Figure 3-1. SO2 concentrations at Eastern Ridge scrubber inlet.

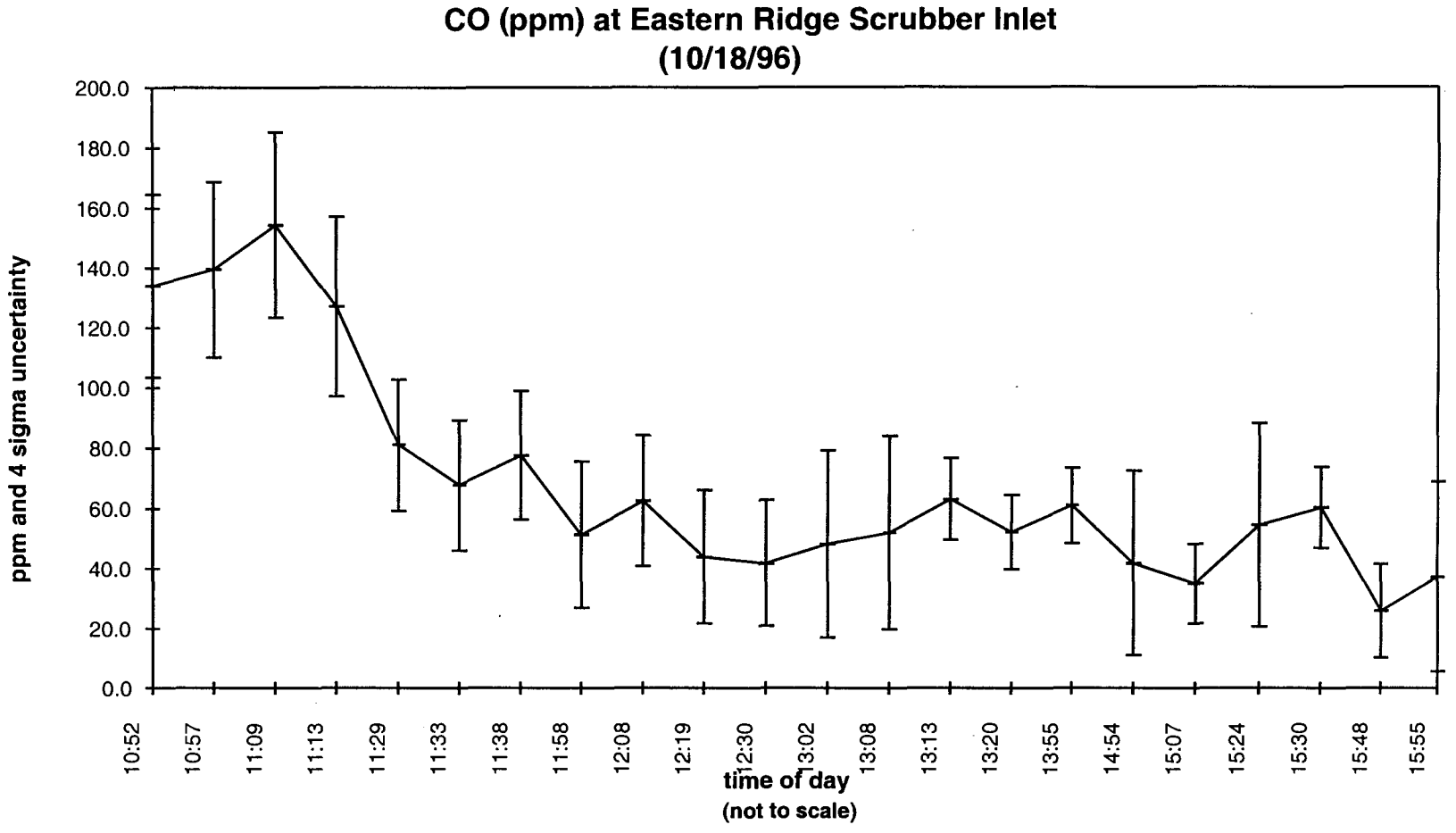



Figure 3-2. CO concentrations at Eastern Ridge scrubber inlet.

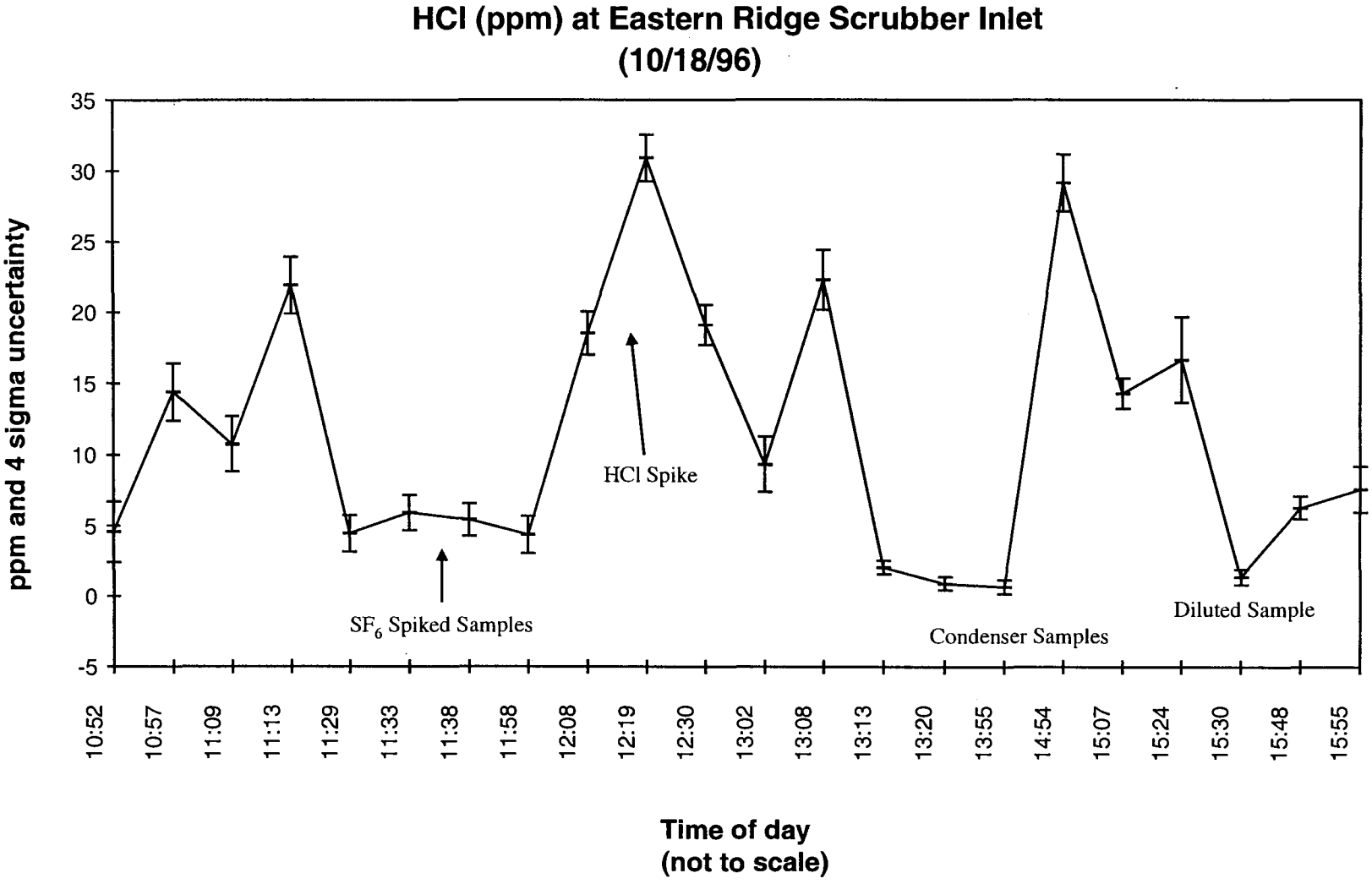



Figure 3-3. HCl concentrations at Eastern Ridge scrubber inlet.

Figure 3-4. SO2 concentrations at Eastern Ridge scrubber outlet.

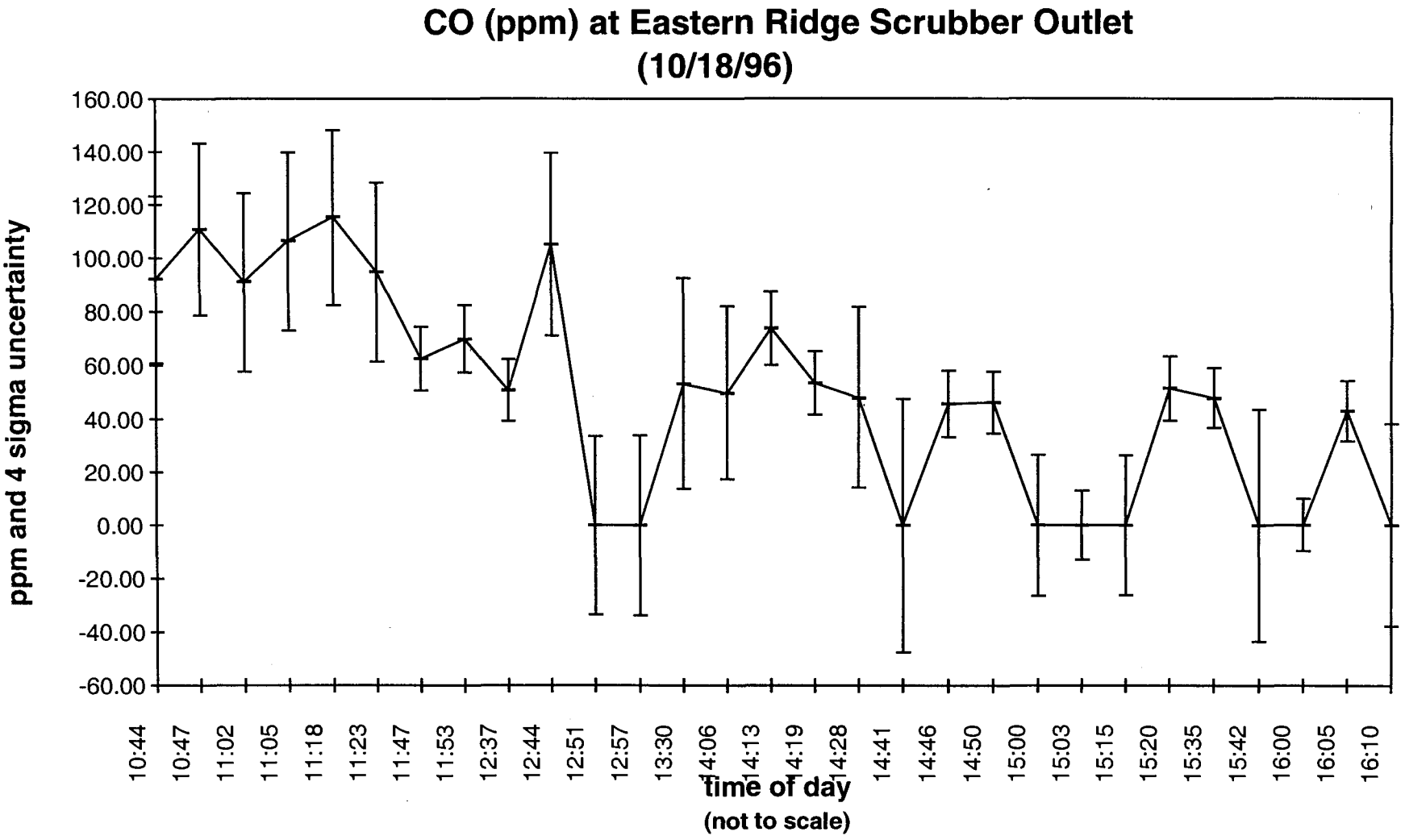



Figure 3-5. CO concentrations at Eastern Ridge scrubber outlet.

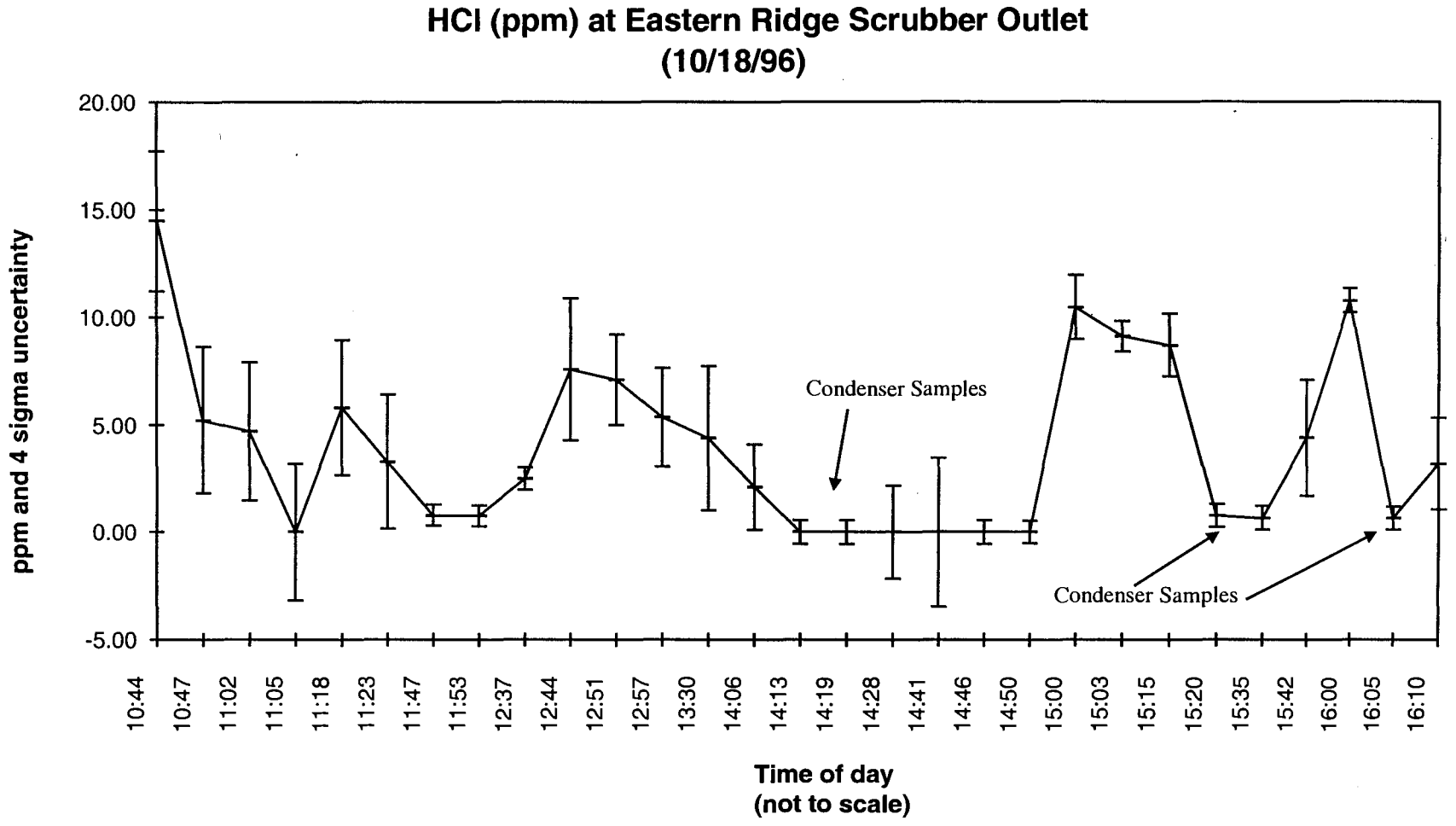



Figure 3-6. HCl concentrations at Eastern Ridge scrubber outlet.

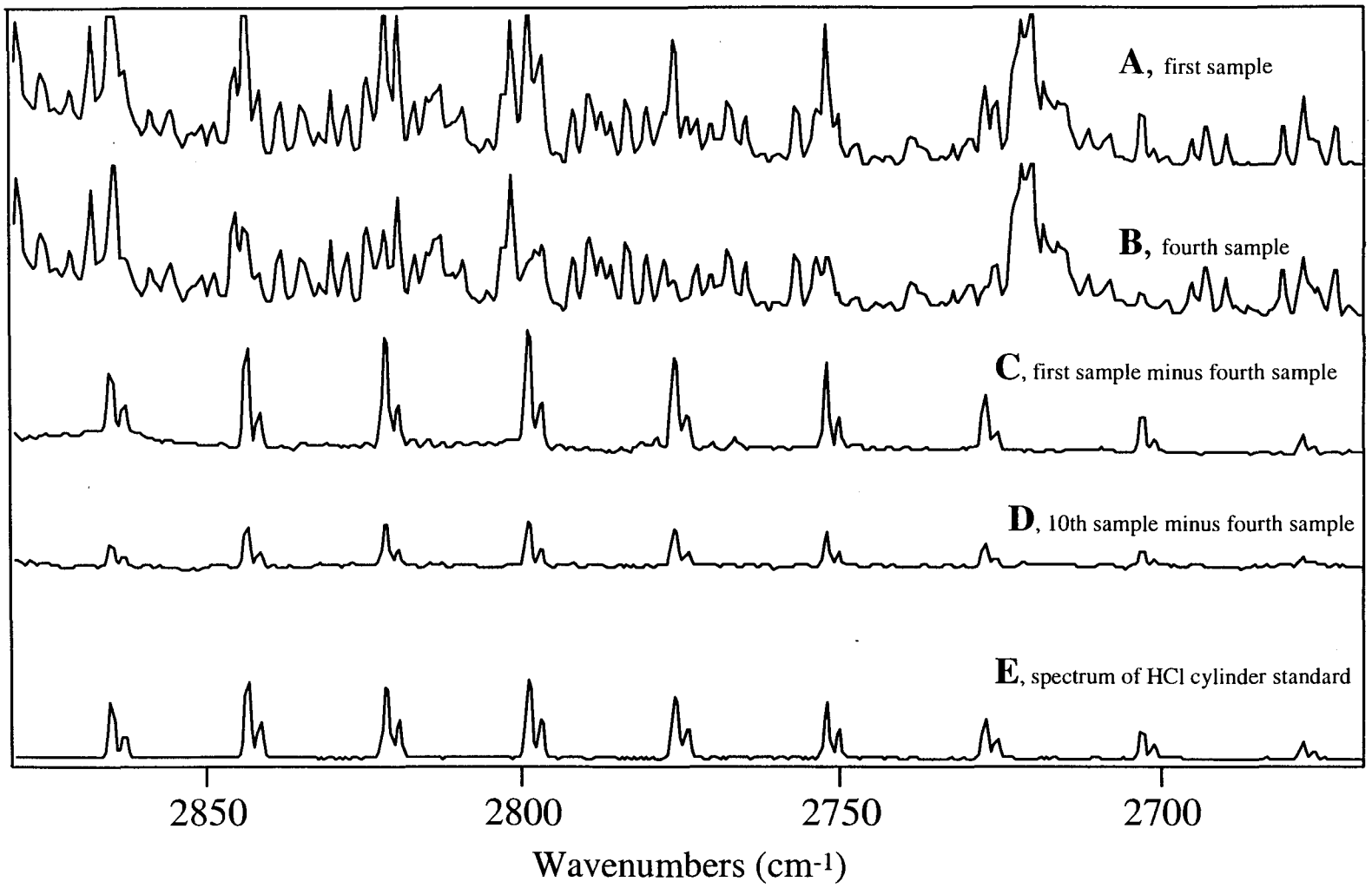



Figure 3-7. Spectra from Eastern Ridge scrubber outlet, 10/18/96. This figure proves the presence of HCl in the unspiked outlet emissions and indicates how the HCl emissions varied during the test run. **A**, "scout201;" **B**, "scout204;" **C**, the result after subtracting "scout204" from "scout201;" **D**, the result after subtracting "scout204" from "scout210." **E**, spectrum of 103 ppm HCl cylinder standard measured at the same path length and temperature. The "standard" spectrum has been scaled by 0.1. All spectra are plotted to the same scale, over a range of 0.035 absorbance units. Refer to Table 3-3 for file names, times, and corresponding HCl concentrations from the output of the spectal analysis.

# 4.0 FTIR TEST PROCEDURES

A heated sample delivery system (Figure 4-1) was used to extract flue gas through a stainless steel probe and transport the flowing sample gas through a heated Teflon sampling line to a heated gas distribution manifold. Valves in the manifold were used to direct the sample flow (or a calibration standard) to the FTIR gas cell.

## 4.1 SAMPLING SYSTEM DESCRIPTION

This description refers to Figure 4-1.

### 4.1.1 Sampling System Components

The sample was extracted through a single port using a 4-ft long, 0.5-in diameter stainless steel probe. Sample was transported through heated 3/8-in Teflon line using a KNF Neuberger heated head sample pump (Model NO35 ST.11I). A Balston particulate filter (holder Model Number 30-25, filter element Model Number 100-25-BH, 99 percent removal efficiency at 0.1 $\mu$m) was connected in-line at the outlet of the sample probe. The sample line was heat wrapped and insulated. Temperature controllers were used to monitor and regulate the sample line temperature at about 350°F.

The sample pump outlet was connected to the sample manifold. The sample stream passed through a secondary Balston particulate filter immediately after entering the manifold box. The manifold is constructed of stainless steel 3/8-in tubing and contains 4-way valves and heated rotameters (0 to 20 LPM) to allow the operator to control sample flow to the FTIR cell. A heated 1/4-in diameter 20-ft long Teflon jumper line connected the manifold to the inlet of the FTIR gas cell. The manifold was maintained at 300° to 310°F.

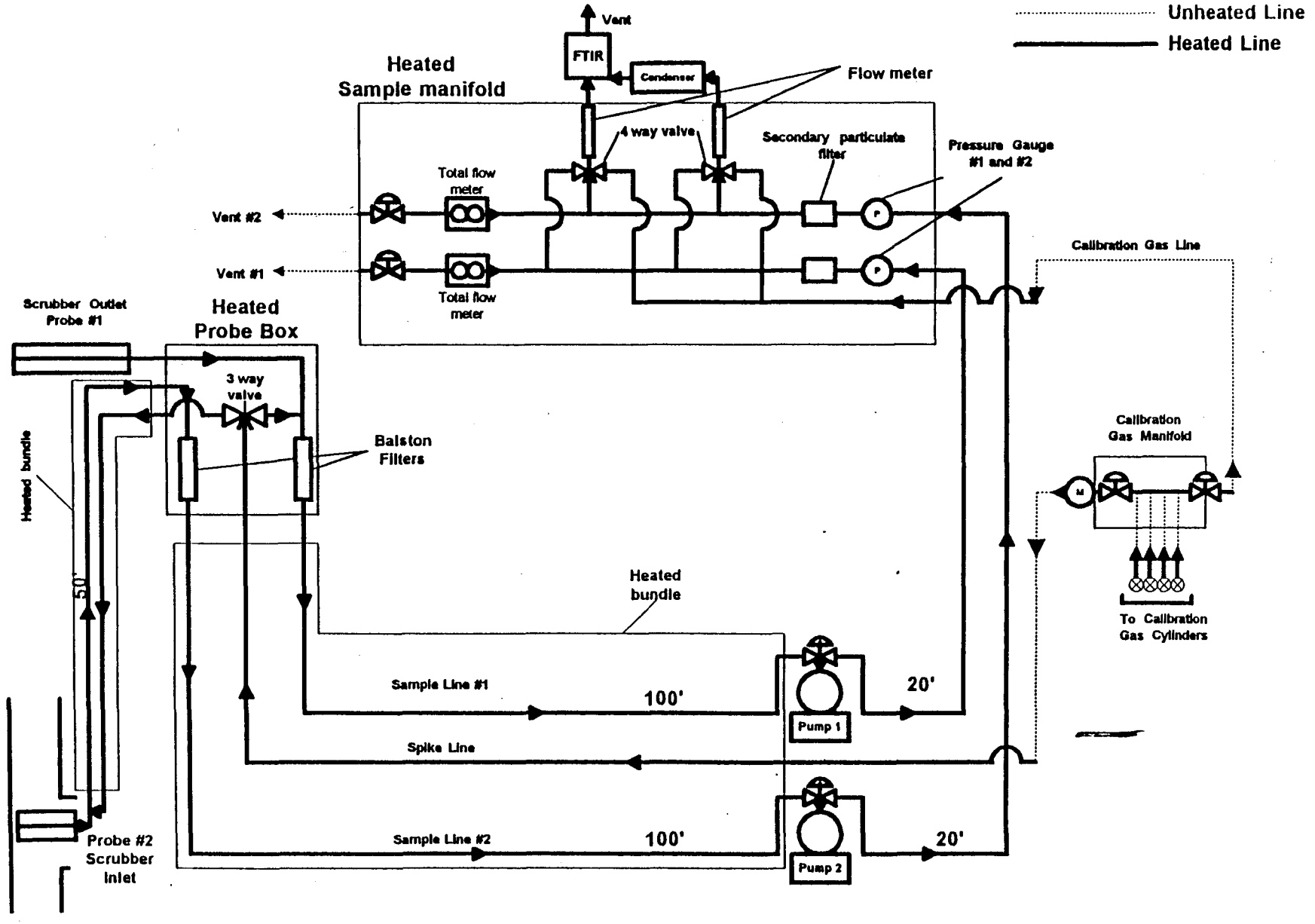



Figure 4-1. FTIR extractive sampling system configuration for test at Eastern Ridge lime plant.

4.1.2 Sample Conditioning

Some samples were passed through a chilled condenser system to remove moisture before going to the FTIR cell. The condenser inlet was connected to a second outlet of the gas distribution manifold through a another heated 1/4-in Teflon. A 4-way valve on the manifold controlled sample flow to the condenser. The condenser outlet was connected by a Teflon line to the inlet of the FTIR gas cell.

Since the condenser is not effective for measuring HCl or other water-soluble compounds, it was not used extensively. The primary benefit of the condenser is in lowering moisture to better reveal spectral features of gas phase compounds, such $NO_x$ and $SO_2$.

4.2 SAMPLING PROCEDURE

This test required two sampling configurations.

4.2.1 Testing Two Locations Simultaneously

The inlet and outlet to the wet scrubber were sampled with the configuration shown in Figure 4-1. A separate sample assembly (probe, line and pump) was used for each location. Both sampling lines were connected to the common sampling manifold. Each line had a pressure gauge at the manifold inlet and a rotameter at the manifold outlet. A turn-valve was used to independently control and monitor the total sample flow through either sample line. Four-way valves, at the manifold outlets leading to the FTIR cell and condenser, could be closed or turned to select gas from either sample.

Both sample lines were contained in the same insulated heated bundle up to scrubber outlet location. The scrubber outlet sample probe was connected directly to the heated probe box that contained the initial particulate filter. The scrubber inlet probe was connected to the same probe box with a 50-ft section of heated sample line. The initial particulate filter for the inlet location was also in the probe box at the end of the 50-ft section of line. The length of the heated bundle from the scrubber outlet to the manifold was 100-ft.

A third, spike, line was contained in the 100-ft heated bundle from the scrubber outlet to the manifold. The spike line carried dry gas standard from the calibration manifold through a mass flow meter (Sierra, ± 1 percent) up to a 3-way in the heated probe box. The valve could be turned to either allow the spike flow to enter the scrubber outlet sample line upstream of the

particulate filter, or direct the spike flow to a "tee" at the back of the scrubber inlet probe. In this way either sample line could be spiked with the HCl standard at a controlled dilution ratio. In this test only the inlet sample was spiked.

The total sample line length was 150-ft from the scrubber inlet location and 100-ft from the scrubber outlet locations to the manifold in the FTIR trailer.

Downstream of the scrubber inlet location the duct divided to pass through two scrubbers, each with its own stack. The stacks were only separated by about 8-ft and were accessible from the same platform. To obtain measurements from both scrubber outlets, the west stack (B) was sampled for the first portion of the sample run, then the probe was moved to the east (A) stack where sampling at the scrubber outlet was resumed with same sample configuration described above.

4.2.2 Testing a Single Location

The hydrator stack was sampled alone. This configuration was the same as that shown in Figure 4-1 for the sample line connection to the scrubber outlet. The spike line and valve configuration for line 1 in Figure 4-1 was also used.

4.3 SAMPLING PROCEDURES

Figure 4-2 is a schematic of the FTIR instrument and connections to the manifold and condenser.

Most of the measurements were performed using a batch sampling procedure to collect a spectrum of a static sample. Some measurements were performed with the sample flowing through the cell. Some samples were diluted in the cell with dry nitrogen and some were passed through a condenser.

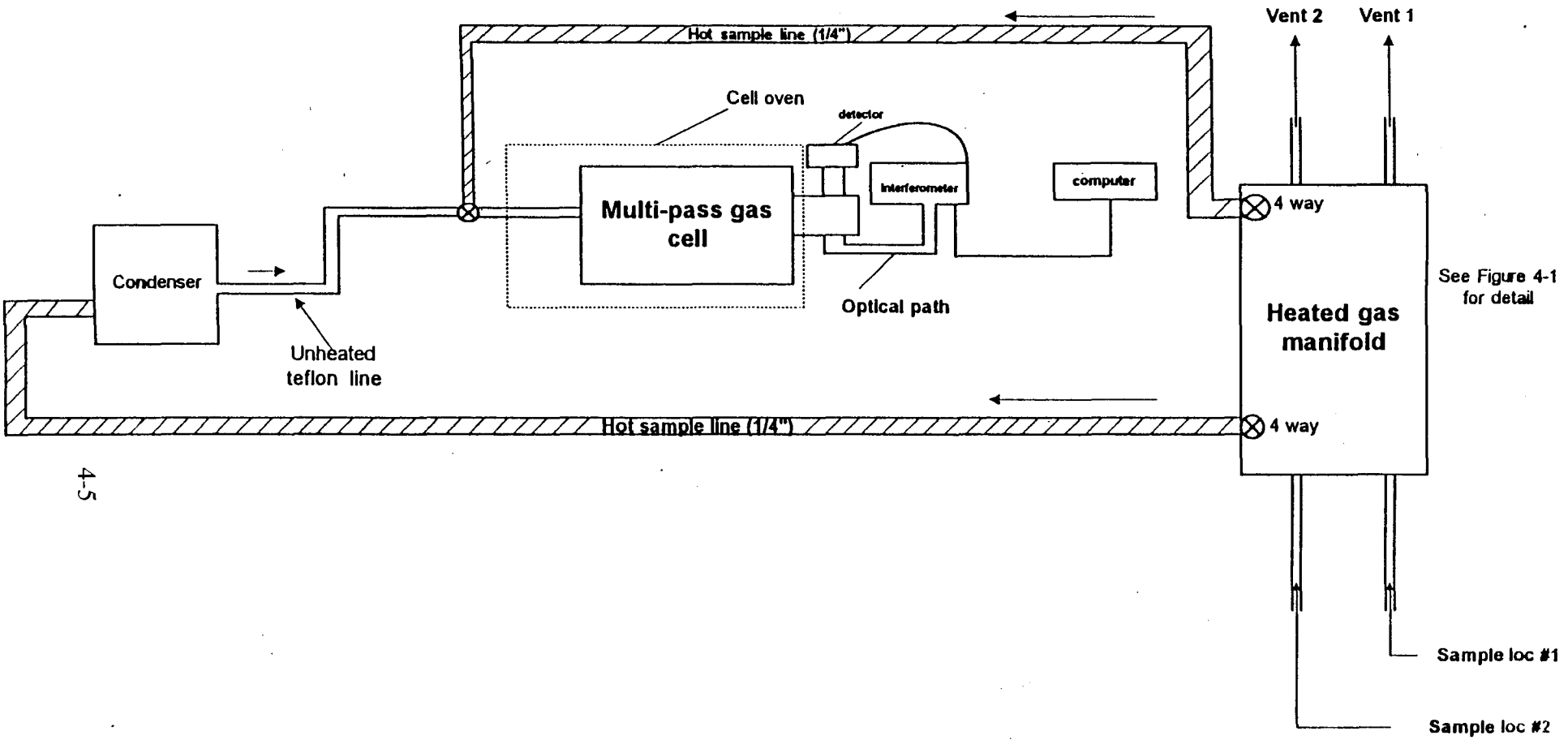



Figure 4-2. FTIR instrument and sampling configuration.

4.3.1 Batch Sampling

The batch sampling procedure was used to collect samples in the FTIR cell.[1] Sample gas was kept continuously flowing through each line and out the manifold vents (Figure 4-1). The 4-way valve was turned to divert a portion of the flow to the FTIR cell. The total flow meter before the vent was monitored to ensure that a positive flow was always directed out the vent during sampling. The cell was filled to above ambient pressure, which was about 720 mm Hg, the 4-way valve was closed, and the cell outlet valve was opened to allow the cell to vent to ambient pressure. The spectrum of the static sample was recorded and then the cell was evacuated for the next sample.

4.3.2 Flow Through Measurements

The cell was filled as in the batch sampling procedure. The sample inlet valve was kept open and the cell outlet valve was also opened to allow gas to pass through the cell. The sample was maintained at ambient pressure by having the outlet valve partially open to the vacuum pump. The inlet sample flow valve was adjusted until the pressure gauge was stable at ambient pressure. The spectrum of the sample was recorded, and then the cell was evacuated for the next sample.

4.3.3 Dilution Samples

Diluting the sample is a procedure for reducing spectral interference from moisture or $CO_2$. This procedure is only effective if the target analyte is present at a high enough concentration to be detected after the dilution. The objective was to dilute the sample to ½ to 1/4 its original concentration.

The cell was partially filled with dry nitrogen and the cell pressure was recorded. Then the cell was filled to ambient pressure with sample gas. The final pressure was recorded, the spectrum of the static sample was measured and the cell was evacuated for the next sample.

4.3.4 Condenser Samples

Directing the sample through a condenser can remove much of the moisture and improve the measurement sensitivity for analytes that pass through the condenser. Analytes that are water soluble, such as HCl, or have low vapor pressures at 32°F cannot be measured using a condenser system.

Sample was diverted to the condenser through a second 4-way valve on the main manifold (Figure 4-2). The valve was turned to direct sample from either location through the condenser. This could be done while untreated sample was sent to the FTIR cell through the other 4-way valve. After flow passed through the condenser for about 10 minutes, a 3-way valve at the cell inlet was turned to allow the condenser sample into the cell. The cell was filled to ambient pressure and the spectrum recorded using the batch sampling procedure.

Before and after sampling a location dry nitrogen was passed through the condenser and into the FTIR cell and a spectrum of the nitrogen was recorded. This was to verify that the condenser was not contaminating the samples.

## 4.4 ANALYTICAL PROCEDURES

Analytical procedures in the EPA FTIR Protocol (Appendix D) were followed.[2] Analytical programs were prepared after the field test was completed. The programs employed automated routines to analyze the spectra using mathematical techniques based on a K-matrix analysis to determine analyte concentrations and sequentially subtract scaled reference spectra from the sample spectra. The subtracted residual baseline spectra was analyzed to estimate uncertainties in the reported concentrations. K-matrix, and other quantitative methods, are described in references 3 and 4. Additional description of the analytical procedures are given in Appendix C.

## 4.5 FTIR SYSTEM

The FTIR system used in this field test was a KVB/Analect RFX-40 interferometer. The gas cell was a heated variable path (D-22H) gas cell from Infrared Analysis, Inc. A path length of 36 laser passes was used for measurements at the scrubber locations and the path length was reduced to 16 passes for measurements at the hydrator stack. A mercury/cadmium/telluride (MCT) liquid nitrogen detector was used with a spectral resolution of 1.0 $cm^{-1}$, the highest resolution of the RFX-40 system.

The path length was measured by shining a He/Ne laser into the cell, and adjusting the mirror tilt until the desired number of laser passes was observed. The number of passes was recorded on the data sheets in Appendix B. The spectrum of an ethylene gas standard was measured before and after each run. These ethylene spectra (calibration transfer standards or

CTS) were then compared to CTS spectra in the EPA FTIR reference spectrum library to determine the path length associated with the number of passes. Details of this procedure and path length results are given in Appendix C.

## 4.6 ANALYTE SPIKING

Hydrogen chloride was an important target analyte. It is reactive and water soluble. Sample flow and temperature influence whether HCl can quantitatively pass through the sampling system to the analyzer. An FTIR instrument is ideally suited to measure spiked samples because many analytes have very distinct infrared spectra and this is especially true of HCl.

The purpose of this procedure is to measure a gas standard directly with the analyzer and compare that measurement to one in a sample that has been spiked with a known concentration of the analyte. Ideally, the spike will comprise about 1/10 or less of the spiked sample.

The spike procedure follows Section 9.2 of EPA Method 320.[1] The $SF_6$ tracer gas was not contained in the same cylinder as the HCl standard. The tracer gas was first spiked from a cylinder standard of 4 ppm $SF_6$ in nitrogen. The total sample flow and the spike flow were continuously monitored and recorded while three separate spiked batch samples were collected and their spectra recorded. The $SF_6$ spike was then turned off and the HCl spike was turned on. The HCl spike flow was set at the same value as the $SF_6$ flow. At least three batch samples spiked with HCl were collected and their spectra recorded while the total sample flow was continuously monitored and recorded. The HCl spike was then turned off and the procedure was repeated with the $SF_6$ standard to collect three more samples.

Only the inlet location was spiked because, unless HCl could be measured at the inlet, it was unlikely to be emitted after passing through the wet scrubber. The sample flow from the inlet was very consistent using the ½-in diameter probe. Since the spike flow rate was also very consistent, the spike ratio was not changing so the procedure of spiking the analyte and the tracer gas separately should have been effective. This is supported by the results of the $SF_6$ spike measurements before and after the run. These results were consistent so variations in the HCl concentration in the (HCl) spiked samples was due to variations in the flue gas HCl concentration.

## 4.7 SCREENING FOR HAPs

Estimated uncertainties for undetected compounds are presented in Tables 3-12 to 3-14.

After analysis, the residual sample spectra were screened for absorbances due to hazardous air pollutants in the EPA FTIR spectral library.

The residual spectra were produced by sequential subtractions of scaled reference spectra. Reference spectra were scaled by a factor equal to the ratio of the calculated sample concentration divided by the reference spectrum concentration (corrected for path length and temperature). The estimated uncertainty is determined primarily by the moisture in the sample gas. Higher moisture results in a higher calculated uncertainty.

The noise level in each analytical region of the residual spectra was taken as the root mean square deviation (RMSD) of the baseline. The RMSD was multiplied by the width (in $cm^{-1}$) of the analytical region. This value was compared to the integrated area in the same region of a reference spectrum of the compound.

The noise was calculated from the equation:

$$RMSD = \left[\left(\frac{1}{n}\right)\Sigma_{i=1}^{n}(A_i - A_M)^2\right]^{\frac{1}{2}} \quad (1)$$

where:

| | | |
|---|---|---|
| RMSD | = | Root mean square deviation in the absorbance values within a region. |
| n | = | Number of absorbance values in the region. |
| $A_i$ | = | Absorbance value of the $i^{th}$ data point in the analytical region. |
| $A_M$ | = | Mean of all the absorbance values in the region. |

The estimated uncertainty for a non-detect is given by:

$$U_{ppm} = \frac{RMSD \; x \; (x_2 - x_1)}{Area_R} \; x \; CON_R \quad (2)$$

where:

| | | |
|---|---|---|
| Uppm | = | Noise related uncertainty in ppm. |
| $X_2$ | = | Upper limit, in $cm^{-1}$, of the analytical region. |
| $X_1$ | = | Lower limit, in $cm^{-1}$, of the analytical region. |
| $Area_R$ | = | Total band area (corrected for path length, temperature, and pressure) in analytical region of reference spectrum. |
| $Con_R$ | = | Reference spectrum concentration. |

This procedure for estimating the uncertainty for an undetected compound usually yields a number that is higher than the actual quantitation limit. This is because no attempt is made to optimize the analytical regions for each compound, nor is the spectral subtraction optimized. (All spectral subtractions are performed, even subtractions that are unnecessary for detecting a particular compound, before the RMSD calculations are performed.) Additionally, band area calculations give a conservative estimate of analyte quantitation limits because the analytical program can usually detect analyte absorbances at lower concentrations than the band area calculations indicate.

# 5.0 SUMMARY OF FTIR QA/QC PROCEDURES

## 5.1 SAMPLING AND TEST CONDITIONS

Before the test, sample lines were cleaned by purging with moist air (250°F). Following this, the lines were checked with nitrogen. This was done by heating the sampling lines to 250°F and then purging with dry nitrogen. The FTIR cell was filled with some of the purging nitrogen and the spectrum of this sample was collected. This single beam spectrum was converted to absorbance using a spectral background of pure nitrogen (99.99 percent) that was taken directly from a cylinder. The lines were checked again on site before sampling. After each sampling run where HCl was detected, the probe was pulled from the stack and ambient air samples were measured to determine the residence time of the HCl in the line.

The run duration for FTIR testing was concurrent with the Method 25A. More than 20 samples were collected and their spectra recorded within the sample run.

Each spectrum was assigned a unique file name and written to the hard disk and a backup disk under that file name when the spectrum was collected. Two copies of each interferogram were also saved under the same filename as the absorbance spectrum using a different file extension. Absorbance spectra and interferograms were saved to different file directories. Two copies of background and calibration interferograms and spectra were also stored on disks to separate directories. A complete copy of all spectra and interferograms was submitted to EPA at the completion of the test before leaving the site.

All of the spectral file names, sampling information, sampling times, sample temperatures and pressures, and the instrument configuration were recorded in writing on data sheets. Copies of these data sheets were submitted to EPA upon completion of the test. Copies of the data

sheets (both the written and transcribed versions) are also included in Appendix B of this report. Minor errors in the original data sheets are corrected in the transcribed version.

Effluent was allowed to flow through the entire sampling system for at least 5 minutes before the first sample was collected. The 20-ft section from the manifold to the FTIR cell was the only part of the sampling system that came in contact with gas from both locations. This 20-ft section of heated line was evacuated after each sample by closing the 4-way valve at the manifold and opening the cell and line to the pump at the cell outlet. This line (and the manifold) was also included in the pre-test leak-check procedure.

FTIR spectra were monitored and a new background spectrum was collected periodically. The data records in Appendix B indicate when new background spectra were collected.

After each change of location, the sample lines were purged with air or nitrogen to clear contamination from the previous run. The lines were checked for contamination by measuring the FTIR spectrum of ambient air samples.

When the condenser was in use, sample was kept constantly flowing through it before a sample was measured. Before switching to the other location, nitrogen was passed through the condenser and a sample of the nitrogen was measured in the FTIR cell.

## 5.2 FTIR SPECTRA

For a detailed description of QA/QC procedures relating to data collection and analysis, refer to the "Protocol For Applying FTIR Spectrometry in Emission Testing" (Appendix D).[2] A spectrum of the calibration transfer standard (CTS) was recorded at the beginning and end of each test run. Positive pressure and vacuum leak checks of the FTIR cell, connection line and sample manifold were performed according to the procedures in references 1 and 2. Leak check results are recorded in Appendix B. Two ethylene standards were used for the CTS. A 20.0 ppm standard was used primarily for the longer path length and a 99.4 ppm standard was used for the shorter path length. Both ethylene standards were measured at each path length. The CTS spectrum provides a check on the operating conditions of the FTIR instrumentation, e.g., spectral resolution and cell path length. Ambient pressure was recorded whenever CTS spectra were collected. Atmospheric pressure measurements were also recorded by the PES test crew. Ambient pressure was about 720 mm Hg (about 28.4 in. Hg).

Two copies of all interferograms, processed backgrounds, sample spectra, and the CTS were stored on separate computer disks. Additional copies of sample and CTS absorbance spectra were also stored for data analysis. Sample absorbance spectra can be regenerated from the raw interferograms, if necessary.

## 5.3 CORRECTIVE ACTIONS

The instrument malfunction described in Section 3.2 was corrected and testing continued.

## 6.0 REFERENCES


1. "Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy," EPA Contract No. 68-D2-0165, Work Assignment 3-08, July, 1996.

2. "Protocol For The Use of FTIR Spectrometry to Perform Extractive Emissions Testing at Industrial Sources," EPA Contract No. 68-D2-0165, Work Assignment 3-12, EMTIC Bulletin Board, September, 1996.

3. "Computer-Assisted Quantitative Infrared Spectroscopy," Gregory L. McClure (ed.), **ASTM Special Publication 934** (ASTM), 1987.

4. "Multivariate Least-Squares Methods Applied to the Quantitative Spectral Analysis of Multicomponent Mixtures," **Applied Spectroscopy**, **39**(10), 73-84, 1985.

5. "Method 301 - Field Validation of Pollutant Measurement Methods from Various Waste Media," **40 CFR Part 63, Appendix A**.

# APPENDIX A.

## ADDITIONAL DATA AND CALCULATIONS

This appendix presents measurements and results from PES. Included are Method 25A results and stack gas measurements conducted during the testing.

EASTERN RIDGE LIME CO.

KILN NO. 2 SCRUBBER INLET DATA

| DATE | 10/16/96 | 10/17/96 | 10/18/96 |
|---|---|---|---|
| $T_s$, °F | 924 | 905 | 950 |
| Moisture % v/v | 11.04 | 10.26 | 8.37 |
| $O_2$ | 3.5 | 2.7 | 5.4 |
| DSCFM | 24,172 | 23,161 | 29,031 |

# Eastern Ridge Lime Company

## Kiln No. 2 Inlet to Scrubbers

**October 16, 1996**

| Calibration Gases | System Calibration |
|---|---|
| 0.0 ppm | 0.80 |
| 30.04 ppm | 29.60 |
| 49.72 ppm | 48.80 |
| 87.86 ppm | 84.00 |

| Correlation | 0.9998234 |
|---|---|
| Slope | 0.9475922 |
| Intercept | 1.0869601 |

| Sampling System Bias |
|---|
| 0.80% |
| 0.80% |
| 2.00% |
| 4.00% |

| Direct Calibration |
|---|
| 0.00 |
| 30.40 |
| 50.80 |
| 88.00 |

| Correlation | 0.999919 |
|---|---|
| Slope | 1.002605 |
| Intercept | 0.285829 |

| Calibration Error |
|---|
| 1.20% |
| 2.17% |

13:20

| Calibration Gases | System Calibration |
|---|---|
| 0.0 ppm | 0.80 |
| 30.04 ppm | 31.20 |
| 49.72 ppm | 51.20 |
| 87.86 ppm | 86.00 |

| Calibration Error |
|---|
| 0.50% |
| 1.30% |

| Correlation | 0.9999027 |
|---|---|
| Slope | 0.9926036 |
| Intercept | 1.1965651 |

| | Post Cal | Drift |
|---|---|---|
| 14:50 | 1.20 | 0.40% |
| | 51.20 | 0.00% |

| | | | | |
|---|---|---|---|---|
| 15:08-15:15 | 3.8 | Corrected | 2.6 | ppm THC (wet basis) |
| 15:15-15:30 | 4.1 | | 2.9 | |
| 15:30-15:45 | 4.1 | | 2.9 | |
| 15:45-16:06 | 4.5 | | 3.3 | |
| 16:06-16:21 | 4.8 | | 3.4 | |
| 16:21-16:36 | 4.7 | | 3.5 | |
| 16:36-16:51 | 4.5 | | 3.3 | |
| 16:51-17:06 | 4.0 | | 2.8 | |
| 17:06-17:21 | 3.4 | | 2.2 | |

| | Post Cal | Drift |
|---|---|---|
| 17:20 | 2.40 | 1.60% |
| | 29.20 | 2.00% |
| | 46.80 | 4.40% |

| Calibration Gases | System Calibration |
|---|---|
| 0.0 ppm | 2.40 |
| 30.04 ppm | 29.20 |
| 49.72 ppm | 46.80 |
| 87.86 ppm | 80.00 |

| Calibration Error |
|---|
| 0.31% |
| 0.67% |

| Correlation | 0.9998739 |
|---|---|
| Slope | 0.8833756 |
| Intercept | 2.5821466 |

| | | | | |
|---|---|---|---|---|
| 17:39-17:45 | 4.9 | Corrected | 2.6 | ppm THC (wet basis) |
| 17:45-18:00 | 4.5 | | 2.2 | |
| 18:00-18:15 | 4.2 | | 1.8 | |
| 18:15-18:30 | 4.1 | | 1.7 | |
| 18:30-18:45 | 3.9 | | 1.5 | |

# Eastern Ridge Lime Company

## Kiln No. 2 Inlet to Scrubbers

| | | |
|---|---|---|
| 18:45-19:00 | 4.3 | 1.9 |
| 19:00-19:15 | 3.4 | 0.9 |
| 19:15-19:30 | 3.9 | 1.4 |
| 19:30-19:45 | 3.6 | 1.2 |
| 19:45-20:00 | 3.7 | 1.3 |
| 20:00-20:05 | 3.8 | 1.4 |

(wet basis)

| | Post Cal | Drift |
|---|---|---|
| 20:10 | 1.20 | 1.20% |
| | 45.60 | 1.20% |

**October 17, 1996**

| Calibration Gases | System Calibration |
|---|---|
| 0.0 ppm | 0.40 |
| 30.04 ppm | 28.40 |
| 49.72 ppm | 47.20 |
| 87.86 ppm | 91.60 |

| Direct Calibration |
|---|
| 0.00 |
| 30.40 |
| 50.80 |
| 87.60 |

| | |
|---|---|
| Correlation | 0.9999313 |
| Slope | 0.9251364 |
| Intercept | 0.6321576 |

Sampling System Bias
0.40%
2.00%
3.60%
6.00%

| | |
|---|---|
| Correlation | 0.999877 |
| Slope | 0.996088 |
| Intercept | 0.375103 |

Calibration Error
1.20%
2.17%

| | Post Cal | Drift |
|---|---|---|
| 11:27 | 0.40 | 0.00% |
| | 48.80 | 0.40% |

| | | | | |
|---|---|---|---|---|
| 11:40-12:00 | 6.3 | Corrected | 6.1 | ppm THC (wet basis) |
| 12:00-12:15 | 6.4 | | 6.2 | |
| 12:15-12:30 | 5.8 | | 5.6 | |
| 12:30-12:45 | 5.7 | | 5.5 | |
| 12:45-13:00 | 6.7 | | 6.6 | |
| 13:00-13:15 | 6.7 | | 6.6 | |
| 13:15-13:30 | 7.2 | | 7.1 | |

| | Post Cal | Drift |
|---|---|---|
| 13:32 | 1.60 | 1.20% |
| | 49.20 | 2.00% |

| | | | | |
|---|---|---|---|---|
| 14:00-14:15 | 9.2 | Corrected | 9.3 | ppm THC (wet basis) |
| 14:15-14:30 | 8.9 | | 8.8 | |
| 14:30-14:45 | 5.9 | | 5.7 | |
| 14:45-15:00 | 6.0 | | 5.8 | |
| 15:00-15:15 | 5.5 | | 5.3 | |
| 15:15-15:30 | 5.3 | | 5.0 | |
| 15:30-15:36 | 5.5 | | 5.3 | |

| | Post Cal | Drift |
|---|---|---|
| 15:38 | 1.60 | 1.20% |
| | 48.40 | 0.80% |

| | | | | |
|---|---|---|---|---|
| 15:45-16:00 | 6.3 | Corrected | 6.1 | ppm THC (wet basis) |
| 16:00-16:15 | 6.3 | | 6.1 | |
| 16:15-16:30 | 6.5 | | 6.3 | |

| | Post Cal | Drift |
|---|---|---|
| 17:06 | 1.60 | 1.20% |
| | 48.80 | 0.40% |

# Eastern Ridge Lime Company
## Kiln No. 2 Inlet to Scrubbers

**October 18, 1996**

| Calibration Gases | System Calibration |
|---|---|
| 0.0 ppm | 0.40 |
| 30.04 ppm | 28.40 |
| 49.72 ppm | 47.20 |
| 87.86 ppm | 80.80 |

| | |
|---|---|
| Correlation | 0.9998347 |
| Slope | 0.9161029 |
| Intercept | 0.8107061 |

| Sampling System Bias |
|---|
| 0.00% |
| 2.00% |
| 3.20% |
| 8.40% |

| Direct Calibration |
|---|
| 0.40 |
| 30.40 |
| 50.40 |
| 87.20 |

| | |
|---|---|
| Correlation | 0.999935 |
| Slope | 0.988685 |
| Intercept | 0.668159 |

| Calibration Error |
|---|
| 1.20% |
| 1.37% |

| | | | | |
|---|---|---|---|---|
| 10:10-10:30 | 8.2 | | 5.9 | ppm THC (wet basis) |
| 10:30-10:45 | 8.0 | | 5.7 | |
| 10:45-11:00 | 5.3 | | 4.9 | |
| 11:00-11:15 | 5.0 | | 4.6 | |
| 11:15-11:30 | 4.7 | | 4.2 | |
| 11:30-11:45 | 4.1 | | 3.6 | |
| 11:45-12:00 | 3.8 | | 3.3 | |
| | Post Cal | Drift | | |
| 12:03 | 0.80 | 0.40% | | |
| | 46.00 | 1.20% | | |
| 12:15-12:30 | 4.9 | | Corrected 4.5 | ppm THC (wet basis) |
| 12:30-12:45 | 4.8 | | 4.4 | |
| 12:45-13:05 | 4.5 | | 4.0 | |
| 13:05-13:15 | 4.6 | | 4.0 | |
| 13:15-13:30 | 4.4 | | 3.9 | |
| 13:30-13:45 | 4.2 | | 3.7 | |
| 13:45-14:00 | 4.2 | | 3.7 | |
| | Post Cal | Drift | | |
| 14:04 | 1.20 | 0.80% | | |
| | 44.40 | 2.80% | | |
| 14:15-14:30 | 6.9 | | Corrected 6.6 | ppm THC (wet basis) |
| 14:30-14:45 | 6.4 | | 6.1 | |
| 14:45-15:00 | 5.9 | | 5.6 | |
| 15:00-15:15 | 5.3 | | 4.9 | |
| 15:15-15:30 | 4.1 | | 3.8 | |
| 15:30-15:45 | 3.9 | | 3.4 | |
| 15:45-16:00 | 3.0 | | 2.4 | |
| 16:00-16:05 | 2.5 | | 1.8 | |
| | Post Cal | Drift | | |
| 16:08 | 0.00 | 0.40% | | |
| | 23.60 | 4.80% | | |
| | 39.20 | 8.00% | | |

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**Summary of Stack Gas Parameters and Test Results**
**Lime Manufacturing Emission Test - Eastern Ridge Lime Company**
**US EPA Test Method 23 - CDD/CDF**
**Kiln No. 2 - Scrubber A Outlet**
**Page 1 of 6**

| | RUN NUMBER | M23-A-1 | M23-A-2 | M23-A-3 | |
|---|---|---|---|---|---|
| | RUN DATE | 10/16/96 | 10/17/96 | 10/18/96 | Average |
| | RUN TIME | 1510-2038 | 1140-1630 | 1100-1543 | |
| | MEASURED DATA | | | | |
| (Y) | Meter Box Correction Factor, Y | 1.008 | 1.008 | 1.008 | 1.008 |
| (dH) | Avg Meter Orifice Pressure, in. H2O | 1.073 | 0.827 | 0.984 | 0.962 |
| (Pbar) | Barometric Pressure, in. Hg | 28.65 | 28.54 | 28.32 | 28.50 |
| (Vm) | Sample Volume, ft³ | 138.188 | 121.991 | 130.841 | 130.340 |
| (Tm) | Average Meter Temperature, °F | 84 | 90 | 98 | 91 |
| (Pg) | Stack Static Pressure, in. H2O | -0.07 | -0.07 | -0.07 | -0.07 |
| (Ts) | Average Stack Temperature, °F | 138 | 135 | 135 | 136 |
| (Vlc) | Condensate Collected, ml | 653.3 | 606.3 | 556.0 | 605.2 |
| (%CO2) | Carbon Dioxide content, % by volume | 21.1 | 23.7 | 21.0 | 21.9 |
| (%O2) | Oxygen content, % by volume | 6.6 | 5.0 | 6.7 | 6.1 |
| (%N2) | Nitrogen content, % by volume | 72.3 | 71.3 | 72.3 | 72.0 |
| (Cp) | Pitot Tube Coefficient | 0.84 | 0.84 | 0.84 | 0.84 |
| (dP) | Avg Sqrt Delta P, (in. H2O)½ | 0.583 | 0.547 | 0.589 | 0.573 |
| (Theta) | Sample Time, min | 240 | 240 | 240 | 240 |
| (Dn) | Nozzle Diameter, in. | 0.257 | 0.247 | 0.247 | 0.250 |
| | CALCULATED DATA | | | | |
| (An) | Nozzle Area, ft² | 0.000360 | 0.000333 | 0.000333 | 0.000342 |
| (Vmstd, cf) | Standard Meter Volume, dscf | 129.658 | 112.781 | 118.347 | 120.262 |
| (Vmstd, cm) | Standard Meter Volume, dscm | 3.652 | 3.177 | 3.334 | 3.388 |
| (Qm) | Average Sampling Rate, dscfm | 0.540 | 0.470 | 0.493 | 0.501 |
| (Ps) | Stack Pressure, in. Hg | 28.64 | 28.53 | 28.31 | 28.50 |
| (%H2O) | Moisture, % by volume | 19.2 | 20.2 | 18.1 | 19.2 |
| (%H2Osat) | Moisture (at saturation), % | 19.3 | 18.1 | 18.1 | 18.5 |
| (Vwstd) | Standard Water Vapor Volume, ft³ | 30.751 | 28.539 | 26.171 | 28.487 |
| (Mfd) | Dry Mole Fraction | 0.81 | 0.82 | 0.82 | 0.82 |
| (Md) | Molecular Weight-dry, lb/lb-mole | 31.64 | 31.99 | 31.63 | 31.75 |
| (Ms) | Molecular Weight-wet, lb/lb-mole | 29.03 | 29.46 | 29.17 | 29.22 |
| (Vs) | Stack Gas Velocity, ft/s | 35.5 | 33.0 | 35.9 | 34.8 |
| (A) | Stack Area, ft² | 12.57 | 12.57 | 12.57 | 12.57 |
| (Qa) | Stack Gas Volumetric flow, acfm | 26,772 | 24,919 | 27,049 | 26,247 |
| (Qs,cmm) | Stack Gas Volumetric flow, dscfm | 18,296 | 17,273 | 18,613 | 18,061 |
| (Qs,cfm) | Stack Gas Volumetric flow, dscmm | 518.1 | 489.1 | 527.1 | 511.4 |
| (I) | Isokinetic Sampling Ratio, % | 103.1 | 102.8 | 100.1 | 102.0 |

**Summary of Stack Gas Parameters and Test Results**
**Lime Manufacturing Emission Test - Eastern Ridge Lime Company**
**US EPA Test Method 29 - Metals and Particulate Matter**
**Kiln No. 2 - Scrubber A Outlet**
**Page 1 of 3**

| | RUN NUMBER | 1 | 2 | 3 | |
|---|---|---|---|---|---|
| | RUN DATE | 10/16/96 | 10/17/96 | 10/18/96 | Average |
| | RUN TIME | 1510-2038 | 1140-1630 | 1100-1548 | |
| | MEASURED DATA | | | | |
| (Y) | Meter Box Correction Factor, Y | 1.009 | 1.009 | 1.009 | 1.009 |
| (dH) | Avg Meter Orifice Pressure, in. H2O | 1.127 | 1.214 | 1.265 | 1.202 |
| (Pbar) | Barometric Pressure, in. Hg | 28.65 | 28.54 | 28.32 | 28.503 |
| (Vm) | Sample Volume, ft³ | 135.203 | 142.503 | 142.643 | 140.116 |
| (Tm) | Average Meter Temperature, °F | 75 | 86 | 77 | 79.021 |
| (Pg) | Stack Static Pressure, in. H2O | -0.07 | -0.10 | -0.10 | -0.090 |
| (Ts) | Average Stack Temperature, °F | 126 | 128 | 129 | 127.410 |
| (Vlc) | Condensate Collected, ml | 632.6 | 632.3 | 615.2 | 626.710 |
| (%CO2) | Carbon Dioxide content, % by volume | 19.0 | 23.7 | 21.0 | 21.233 |
| (%O2) | Oxygen content, % by volume | 7.8 | 5.0 | 6.7 | 6.500 |
| (%N2) | Nitrogen content, % by volume | 73.2 | 71.3 | 72.3 | 72.267 |
| (Cp) | Pitot Tube Coefficient | 0.84 | 0.84 | 0.84 | 0.840 |
| (dP) | Avg Sqrt Delta P, (in. H2O)½ | 0.5706 | 0.5680 | 0.6210 | 0.587 |
| (Theta) | Sample Time, min | 240 | 240 | 240 | 240.000 |
| (Dn) | Nozzle Diameter, in. | 0.254 | 0.259 | 0.250 | 0.254 |
| | CALCULATED DATA | | | | |
| (An) | Nozzle Area, square feet | 0.00035 | 0.00037 | 0.00034 | 0.000 |
| (Vmstd) | Standard Meter Volume, ft³ | 129.352 | 133.065 | 134.380 | 132.266 |
| (Ps) | Stack Pressure, inches Hg | 28.64 | 28.53 | 28.31 | 28.497 |
| (%H2O) | Moisture, % | 18.7 | 18.3 | 17.7 | 18.240 |
| (%H2Osat) | Moisture (at saturation), % | 14.1 | 14.9 | 15.4 | 14.796 |
| (Vwstd) | Standard Water Vapor Volume, ft³ | 29.778 | 29.762 | 28.957 | 29.499 |
| (Mfd) | Dry Mole Fraction | 0.859 | 0.851 | 0.846 | 0.852 |
| (Md) | Molecular Weight-dry, lb/lb-mole | 31.35 | 31.99 | 31.63 | 31.657 |
| (Ms) | Molecular Weight-wet, lb/lb-mole | 26.94 | 27.23 | 26.75 | 26.972 |
| (Vs) | Velocity, ft/s | 35.7 | 35.5 | 39.3 | 36.833 |
| (A) | Stack Area, ft² | 12.57 | 12.57 | 12.57 | 12.570 |
| (Qa) | Volumetric flow, acfm | 26,923 | 26,759 | 29,655 | 27779 |
| (Qs) | Volumetric flow, dscfm | 19,959 | 19,503 | 21,275 | 20245 |
| (I) | Isokinetic Rate, % | 96.5 | 97.7 | 97.1 | 97.082 |

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**Summary of Stack Gas Parameters and Test Results**
**Lime Manufacturing Emission Test - Eastern Ridge Lime Company**
**US EPA Test Method 23 - CDD/CDF**
**Kiln No. 2 - Scrubber B Outlet**
**Page 1 of 6**

| | RUN NUMBER | M23-B1 | M23-B2 | M23-B3 | |
|---|---|---|---|---|---|
| | RUN DATE | 10/16/96 | 10/17/96 | 10/18/96 | Average |
| | RUN TIME | 1511-2027 | 1140-1630 | 1100-1540 | |
| | MEASURED DATA | | | | |
| (Y) | Meter Box Correction Factor, Y | 1.003 | 1.003 | 1.003 | 1.003 |
| (dH) | Avg Meter Orifice Pressure, in. H2O | 2.292 | 0.808 | 1.476 | 1.525 |
| (Pbar) | Barometric Pressure, in. Hg | 28.65 | 28.54 | 28.30 | 28.50 |
| (Vm) | Sample Volume, ft³ | 187.909 | 116.621 | 151.944 | 152.158 |
| (Tm) | Average Meter Temperature, °F | 94 | 95 | 81 | 90 |
| (Pg) | Stack Static Pressure, in. H2O | -0.06 | 0.05 | 0.12 | 0.04 |
| (Ts) | Average Stack Temperature, °F | 135 | 131 | 134 | 133 |
| (Vlc) | Condensate Collected, ml | 783.0 | 415.4 | 614.4 | 604.3 |
| (%CO2) | Carbon Dioxide content, % by volume | 19.0 | 20.0 | 19.7 | 19.6 |
| (%O2) | Oxygen content, % by volume | 7.8 | 7.7 | 7.6 | 7.7 |
| (%N2) | Nitrogen content, % by volume | 73.2 | 72.3 | 72.7 | 72.7 |
| (Cp) | Pitot Tube Coefficient | 0.84 | 0.84 | 0.84 | 0.84 |
| (dP) | Avg Sqrt Delta P, (in. H2O)½ | 0.363 | 0.312 | 0.425 | 0.367 |
| (Theta) | Sample Time, min | 240 | 240 | 240 | 240 |
| (Dn) | Nozzle Diameter, in. | 0.375 | 0.310 | 0.310 | 0.332 |
| | CALCULATED DATA | | | | |
| (An) | Nozzle Area, ft² | 0.000767 | 0.000524 | 0.000524 | 0.000605 |
| (Vmstd, cf) | Standard Meter Volume, dscf | 172.998 | 106.346 | 141.244 | 140.196 |
| (Vmstd, cm) | Standard Meter Volume, dscm | 4.873 | 2.996 | 3.979 | 3.949 |
| (Qm) | Average Sampling Rate, dscfm | 0.721 | 0.443 | 0.589 | 0.584 |
| (Ps) | Stack Pressure, in. Hg | 28.65 | 28.54 | 28.31 | 28.50 |
| (%H2O) | Moisture, % by volume | 17.6 | 15.5 | 17.0 | 16.7 |
| (%H2Osat) | Moisture (at saturation), % | 17.8 | 16.3 | 17.6 | 17.3 |
| (Vwstd) | Standard Water Vapor Volume, ft³ | 36.856 | 19.553 | 28.920 | 28.443 |
| (Mfd) | Dry Mole Fraction | 0.82 | 0.84 | 0.83 | 0.83 |
| (Md) | Molecular Weight-dry, lb/lb-mole | 31.35 | 31.51 | 31.46 | 31.44 |
| (Ms) | Molecular Weight-wet, lb/lb-mole | 29.01 | 29.41 | 29.17 | 29.20 |
| (Vs) | Stack Gas Velocity, ft/s | 22.1 | 18.8 | 25.9 | 22.3 |
| (A) | Stack Area, ft² | 12.57 | 12.57 | 12.57 | 12.57 |
| (Qa) | Stack Gas Volumetric flow, acfm | 16,653 | 14,168 | 19,530 | 16,783 |
| (Qs,cmm) | Stack Gas Volumetric flow, dscfm | 11,667 | 10,192 | 13,633 | 11,831 |
| (Qs,cfm) | Stack Gas Volumetric flow, dscmm | 330.4 | 288.6 | 386.0 | 335.0 |
| (I) | Isokinetic Sampling Ratio, % | 101.3 | 104.3 | 103.5 | 103.0 |

**Summary of Stack Gas Parameters and Test Results**
**Lime Manufacturing Emission Test - Eastern Ridge Lime Company**
**US EPA Test Method 29 - Metals and Particulate Matter**
**Kiln No. 2 - Scrubber B Outlet**
**Page 1 of 3**

| | | | | | |
|---|---|---|---|---|---|
| | RUN NUMBER | 1 | 2 | 3 | |
| | RUN DATE | 10/16/96 | 10/17/96 | 10/18/96 | Average |
| | RUN TIME | 1514-2037 | 1140-1630 | 1100-1550 | |
| | MEASURED DATA | | | | |
| (Y) | Meter Box Correction Factor, Y | 1.003 | 1.003 | 1.003 | |
| (dH) | Avg Meter Orifice Pressure, in. H2O | 2.004 | 0.670 | 1.043 | |
| (Pbar) | Barometric Pressure, in. Hg | 28.65 | 28.54 | 28.30 | |
| (Vm) | Sample Volume, ft³ | 187.128 | 113.837 | 132.495 | |
| (Tm) | Average Meter Temperature, °F | 94 | 97 | 85 | |
| (Pg) | Stack Static Pressure, in. H2O | -0.06 | 0.05 | 0.12 | |
| (Ts) | Average Stack Temperature, °F | 135 | 130 | 133 | |
| (Vlc) | Condensate Collected, ml | 776.9 | 390.4 | 520.7 | |
| (%CO2) | Carbon Dioxide content, % by volume | 19.0 | 20.0 | 19.7 | |
| (%O2) | Oxygen content, % by volume | 7.8 | 7.7 | 7.6 | |
| (%N2) | Nitrogen content, % by volume | 73.2 | 72.3 | 72.7 | |
| (Cp) | Pitot Tube Coefficient | 0.84 | 0.84 | 0.84 | |
| (dP) | Avg Sqrt Delta P, (in. H2O)½ | 0.3587 | 0.3047 | 0.3745 | |
| (Theta) | Sample Time, min | 240 | 240 | 240 | |
| (Dn) | Nozzle Diameter, in. | 0.378 | 0.310 | 0.310 | |
| | CALCULATED DATA | | | | |
| (An) | Nozzle Area, square feet | 0.00078 | 0.00052 | 0.00052 | |
| (Vmstd) | Standard Meter Volume, ft³ | 172.068 | 103.417 | 122.085 | |
| (Ps) | Stack Pressure, inches Hg | 28.65 | 28.54 | 28.31 | |
| (%H2O) | Moisture, % | 17.5 | 15.1 | 16.7 | |
| (%H2Osat) | Moisture (at saturation), % | 18.2 | 16.0 | 17.5 | |
| (Vwstd) | Standard Water Vapor Volume, ft³ | 36.569 | 18.376 | 24.509 | |
| (Mfd) | Dry Mole Fraction | 0.825 | 0.849 | 0.833 | |
| (Md) | Molecular Weight-dry, lb/lb-mole | 31.35 | 31.51 | 31.46 | |
| (Ms) | Molecular Weight-wet, lb/lb-mole | 25.86 | 26.75 | 26.20 | |
| (Vs) | Velocity, ft/s | 23.1 | 19.2 | 24.1 | |
| (A) | Stack Area, ft² | 12.57 | 12.57 | 12.57 | |
| (Qa) | Volumetric flow, acfm | 17,419 | 14,507 | 18,145 | |
| (Qs) | Volumetric flow, dscfm | 12,192 | 10,507 | 12,717 | |
| (I) | Isokinetic Rate, % | 94.9 | 98.4 | 96.0 | |

# Eastern Ridge Lime Company

## Kiln No. 2 Outlet of Scrubbers

**October 16, 1996**

| | Scrubber A | Scrubber B | |
|---|---|---|---|
| Calibration Gases | System Calibration | System Calibration | Direct Calibration |
| 0.0 ppm | 2.35 | 0.80 | 0.00 |
| 30.04 ppm | 30.25 | 30.00 | 30.40 |
| 49.72 ppm | 49.36 | 49.20 | 50.80 |
| 87.88 ppm | 83.66 | 84.40 | 88.00 |
| | Correlation 0.999897 | Correlation 0.999886 | Correlation 0.99992 |
| | Slope 0.9271117 | Slope 0.8518108 | Slope 1.00261 |
| | Intercept 2.5593823 | Intercept 1.2143665 | Intercept 0.28583 |
| | Sampling System Bias | Sampling System Bias | Calibration Error |
| | 2.35% | 0.80% | |
| | 0.15% | 0.40% | 1.20% |
| | 1.42% | 1.60% | 2.17% |
| | 4.34% | 3.60% | |

| | Post Cal | Drift | Post Cal | Drift |
|---|---|---|---|---|
| 13:00 | 1.60 | 0.75% | 1.60 | 0.80% |
| | 50.00 | 0.62% | 50.40 | 1.20% |
| | Post Cal | Drift | Post Cal | Drift |
| 14:57 | 2.00 | 0.35% | 1.60 | 0.80% |
| | 49.60 | 0.22% | 50.00 | 0.80% |

| | | | | | | |
|---|---|---|---|---|---|---|
| 15:15-15:30 | 4.1 | Corrected | A | 1.7 | ppm THC | (wet basis) |
| 15:30-15:45 | 5.1 | | B | 4.1 | | |
| 15:45-16:06 | 5.7 | | A | 3.4 | | |
| 16:06-16:21 | 5.1 | | B | 5.1 | | |
| 16:21-16:36 | 5.9 | | A | 3.6 | | |
| 16:36-16:51 | 5.8 | | B | 4.8 | | |
| 16:51-17:06 | 5.7 | | A | 3.4 | | |
| 17:06-17:21 | 4.4 | | B | 3.3 | | |

| | Post Cal | Drift | Post Cal | Drift |
|---|---|---|---|---|
| 17:36 | 2.40 | 0.05% | 1.60 | 0.80% |
| | 44.80 | 4.58% | 48.40 | 0.80% |
| | 28.40 | 1.85% | | |

| Calibration Gases | System Calibration |
|---|---|
| 0.0 ppm | 2.40 |
| 30.04 ppm | 28.40 |
| 49.72 ppm | 44.80 |
| 87.88 ppm | 77.20 |
| | Calibration Error |
| | 1.13% |
| | 0.11% |
| | Correlation 0.9999797 |
| | Slope 0.8502501 |
| | Intercept 2.5702577 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 18:15-18:30 | 5.0 | Corrected | A | 2.9 | ppm THC | (wet basis) |
| 18:30-18:45 | 6.1 | | B | 5.1 | | |
| 18:45-19:00 | 4.8 | | A | 2.8 | | |
| 19:00-19:15 | 4.6 | | B | 3.6 | | |
| 19:15-19:30 | 4.9 | | A | 2.7 | | |
| 19:30-19:45 | 4.8 | | B | 3.8 | | |
| 19:45-20:00 | 4.7 | | A | 2.5 | | |
| 20:00-20:15 | 4.4 | | B | 3.3 | | |

| | Post Cal | Drift | Post Cal | Drift |
|---|---|---|---|---|
| 20:20 | 1.60 | 0.80% | 1.20 | 0.40% |
| | 44.00 | 0.80% | 44.40 | 4.80% |
| | | | 27.60 | 2.40% |

# Eastern Ridge Lime Company

## Kiln No. 2 Outlet of Scrubbers

**October 17, 1996**

| | Scrubber A | Scrubber B | |
|---|---|---|---|
| Calibration Gases | System Calibration | System Calibration | Direct Calibration |
| 0.0 ppm | 0.80 | 0.80 | 0.00 |
| 30.04 ppm | 29.60 | 30.00 | 30.40 |
| 49.72 ppm | 48.40 | 49.20 | 50.40 |
| 87.86 ppm | 83.20 | 84.40 | 87.20 |
| | Correlation 0.9999028 | Correlation 0.999686 | Correlation 0.9968 |
| | Slope 0.9378908 | Slope 0.9518108 | Slope 0.9928 |
| | Intercept 1.1976962 | Intercept 1.2143686 | Intercept 0.39657 |
| | Sampling System Bias | Sampling System Bias | Calibration Error |
| | 0.80% | 0.80% | |
| | 0.80% | 0.40% | 1.20% |
| | 2.00% | 1.20% | 1.37% |
| | 4.00% | 2.80% | |

| | Post Cal | Drift | Post Cal | Drift |
|---|---|---|---|---|
| 11:10 | 1.20 | 0.40% | 0.80 | 0.00% |
| | 45.80 | 2.80% | 48.80 | 0.40% |

| Calibration Gases | System Calibration |
|---|---|
| 0.0 ppm | 1.20 |
| 30.04 ppm | 29.40 |
| 49.72 ppm | 45.60 |
| 87.86 ppm | 78.80 |
| | Calibration Error |
| | 1.39% |
| | 0.47% |
| Correlation | 0.9999455 |
| Slope | 0.8922094 |
| Intercept | 1.5310148 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 11:40-12:00 | 8.4 | | Corrected | A | 5.5 | ppm THC (wet basis) |
| 12:00-12:15 | | | | B | | |
| 12:15-12:30 | 5.7 | | | B | 4.7 | |
| 12:30-12:45 | 7.1 | | | A | 6.3 | |
| 12:45-13:00 | 5.8 | | | B | 4.8 | |
| 13:00-13:15 | 7.7 | | | A | 7.0 | |
| 13:15-13:30 | 8.5 | | | B | 5.6 | |

| | Post Cal | Drift | Post Cal | Drift |
|---|---|---|---|---|
| 13:38 | 1.60 | 0.40% | 1.20 | 0.40% |
| | 44.00 | 1.60% | 44.40 | 4.80% |
| | | | 27.80 | 2.40% |

| | | | | | | |
|---|---|---|---|---|---|---|
| 14:00-14:15 | 9.9 | | Corrected | A | 9.5 | ppm THC (wet basis) |
| 14:15-14:30 | 7.5 | | | B | 8.6 | |
| 14:30-14:45 | 7.3 | | | A | 8.5 | |
| 14:45-15:00 | 8.4 | | | B | 5.4 | |
| 15:00-15:15 | 6.9 | | | A | 8.0 | |
| 15:15-15:30 | 5.5 | | | B | 4.6 | |
| 15:30-15:45 | 8.0 | | | A | 9.1 | |
| 15:45-16:00 | 5.2 | | | B | 4.2 | |
| 16:00-16:15 | 6.2 | | | A | 5.3 | |
| 16:15-16:30 | 5.5 | | | B | 4.5 | |

| | Post Cal | Drift | Post Cal | Drift |
|---|---|---|---|---|
| 16:35 | 2.40 | 1.20% | 1.60 | 0.80% |
| | 42.80 | 2.80% | 46.00 | 3.20% |
| | 27.20 | 1.20% | 28.40 | 1.60% |

# Eastern Ridge Lime Company

## Kiln No. 2 Outlet of Scrubbers

**October 18, 1996**

| Calibration Gases | Scrubber A System Calibration | Scrubber B System Calibration | Direct Calibration |
|---|---|---|---|
| 0.0 ppm | 1.20 | 1.20 | 0.40 |
| 30.04 ppm | 29.60 | 29.60 | 29.60 |
| 49.72 ppm | 48.00 | 48.80 | 49.60 |
| 87.86 ppm | 82.40 | 83.20 | 85.60 |

| | | | | | |
|---|---|---|---|---|---|
| Correlation | 0.9999174 | Correlation | 0.9999174 | Correlation | 0.99991 |
| Slope | 0.9239703 | Slope | 0.93454 | Slope | 0.97141 |
| Intercept | 1.5610258 | Intercept | 1.5361022 | Intercept | 0.59269 |
| Sampling System Bias | | Sampling System Bias | | Calibration Error | |
| 0.80% | | 0.80% | | | |
| 0.00% | | 0.00% | | 1.46% | |
| 1.60% | | 0.80% | | 0.24% | |
| 3.20% | | 2.40% | | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| 10:10-10:30 | 6.1 | | Corrected | A | 4.9 | ppm THC (wet basis) |
| 10:30-10:45 | 5.9 | | | B | 4.7 | |
| 10:45-11:00 | 6.2 | | | A | 5.0 | |
| 11:00-11:15 | 5.6 | | | B | 4.3 | |
| 11:15-11:30 | 6.3 | | | A | 5.1 | |
| 11:30-11:45 | 4.9 | | | B | 3.6 | |
| 11:45-12:00 | 5.2 | | | A | 3.9 | |
| 12:00-12:15 | 4.6 | | | B | 3.3 | |

| | Post Cal | Drift | Post Cal | Drift |
|---|---|---|---|---|
| 12:20 | 1.60 | 0.40% | 1.60 | 0.40% |
| | 26.80 | 2.80% | 27.20 | 2.40% |
| | 42.00 | 6.00% | 44.00 | 4.80% |

| Calibration Gases | System Calibration | System Calibration |
|---|---|---|
| 0.0 ppm | 1.60 | 1.60 |
| 30.04 ppm | 26.80 | 27.20 |
| 49.72 ppm | 42.00 | 44.00 |
| 87.86 ppm | 78.40 | 78.40 |
| | Calibration Error | Calibration Error |
| | 0.67% | 0.88% |
| | 3.16% | 1.72% |
| Correlation | 0.9995726 | Correlation 0.9998681 |
| Slope | 0.8487419 | Slope 0.874 |
| Intercept | 1.1334589 | Intercept 1.1750281 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 13:05-13:15 | 5.6 | | Corrected | A | 5.3 | ppm THC (wet basis) |
| 13:15-13:30 | 5.6 | | | A | 5.3 | |
| 13:30-13:45 | 4.7 | | | B | 4.0 | |
| 13:45-14:00 | 5.5 | | | A | 5.1 | |
| 14:00-14:15 | 4.6 | | | B | 3.9 | |
| 14:15-14:30 | 6.3 | | | A | 6.1 | |
| 14:30-14:45 | 4.8 | | | B | 4.1 | |

| | Post Cal | Drift | Post Cal | Drift |
|---|---|---|---|---|
| 14:50 | 1.20 | 0.40% | 0.80 | 0.80% |
| | 26.40 | 0.40% | 27.20 | 0.00% |
| | 43.20 | 1.20% | 44.00 | 0.00% |

| | | | | | | |
|---|---|---|---|---|---|---|
| 15:15-15:30 | 5.6 | | Corrected | A | 5.3 | ppm THC (wet basis) |
| 15:30-15:45 | 4.8 | | | B | 4.1 | |
| 15:45-16:00 | 5.1 | | | A | 4.7 | |
| 16:00-16:15 | 4.0 | | | B | 3.2 | |

| | Post Cal | Drift | Post Cal | Drift |
|---|---|---|---|---|
| 16:18 | 0.80 | 0.80% | 0.40 | 1.20% |
| | 24.00 | 2.80% | 26.00 | 1.20% |
| | 40.00 | 2.00% | 42.40 | 1.60% |

**Summary of Stack Gas Parameters and Test Results**
**Lime Manufacturing Emission Test - Eastern Ridge Lime Company**
**US EPA Test Method 29 - Metals and Particulate Matter**
**Kiln No. 2 - Hydrator Stack**
**Page 1 of 3**

| | RUN NUMBER | M29-4 | M29-5 | M29-6 | M29-7 |
|---|---|---|---|---|---|
| | RUN DATE | 10/19/96 | 10/19/96 | 10/20/96 | 10/20/96 |
| | RUN TIME | 1100-1306 | 1339-1541 | 1008-1213 | 1233-1436 |
| | MEASURED DATA | | | | |
| (Y) | Meter Box Correction Factor, Y | 1.003 | 1.003 | 1.003 | 1.003 |
| (dH) | Avg Meter Orifice Pressure, in. H2O | 1.021 | 0.683 | 0.442 | 0.566 |
| (Pbar) | Barometric Pressure, in. Hg | 28.25 | 28.25 | 28.26 | 28.260 |
| (Vm) | Sample Volume, ft³ | 68.258 | 55.512 | 44.722 | 52.934 |
| (Tm) | Average Meter Temperature, °F | 81 | 82 | 70 | 73.875 |
| (Pg) | Stack Static Pressure, in. H2O | 0.18 | 0.17 | 0.18 | 0.150 |
| (Ts) | Average Stack Temperature, °F | 184 | 185 | 185 | 185.625 |
| (Vlc) | Condensate Collected, ml | 1858.8 | 1601.1 | 1155.4 | 1495.500 |
| (%CO2) | Carbon Dioxide content, % by volume | 0.0 | 0.0 | 0.0 | 0.000 |
| (%O2) | Oxygen content, % by volume | 21.0 | 21.0 | 21.0 | 21.000 |
| (%N2) | Nitrogen content, % by volume | 79.0 | 79.0 | 79.0 | 79.000 |
| (Cp) | Pitot Tube Coefficient | 0.84 | 0.84 | 0.84 | 0.840 |
| (dP) | Avg Sqrt Delta P, (in. H2O)½ | 0.2666 | 0.2839 | 0.2519 | 0.286 |
| (Theta) | Sample Time, min | 120 | 120 | 120 | 120.000 |
| (Dn) | Nozzle Diameter, in. | 0.437 | 0.439 | 0.437 | 0.439 |
| | CALCULATED DATA | | | | |
| (An) | Nozzle Area, square feet | 0.00104 | 0.00105 | 0.00104 | 0.001 |
| (Vmstd) | Standard Meter Volume, ft³ | 65.615 | 51.301 | 42.234 | 49.648 |
| (Ps) | Stack Pressure, inches Hg | 28.26 | 28.26 | 28.27 | 28.271 |
| (%H2O) | Moisture, % | 57.1 | 59.5 | 56.3 | 58.641 |
| (%H2Osat) | Moisture (at saturation), % | 59.2 | 60.4 | 60.3 | 61.083 |
| (Vwstd) | Standard Water Vapor Volume, ft³ | 87.494 | 75.364 | 54.385 | 70.393 |
| (Mfd) | Dry Mole Fraction | 0.429 | 0.405 | 0.437 | 1.000 |
| (Md) | Molecular Weight-dry, lb/lb-mole | 28.84 | 28.84 | 28.84 | 28.840 |
| (Ms) | Molecular Weight-wet, lb/lb-mole | 12.36 | 11.68 | 12.61 | 28.840 |
| (Vs) | Velocity, ft/s | 28.0 | 28.5 | 24.3 | 18.268 |
| (A) | Stack Area, ft² | 2.76 | 2.76 | 2.76 | 2.761 |
| (Qa) | Volumetric flow, acfm | 4,306 | 4,721 | 4,032 | 3026 |
| (Qs) | Volumetric flow, dscfm | 1,428 | 1,478 | 1,363 | 2338 |
| (I) | Isokinetic Rate, % | 101.5 | 76.0 | 68.5 | 46.500 |

# APPENDIX B.

# FIELD DATA RECORDS

Data Sheet: FTIR Background and Calibration Spectra: Eastern Ridge Lime Kiln. EPA Work Assignment 4-01.

| Date | Time | File Name | Path | Location/Notes | #scans | Res (cm-1) | Cell temp (F) | Pressure | BKG | Apod |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | |
| 10/15/96 | 17:00 | | | *Leak check cell & manifold under pressure of 931 torr. Held steady for one minute. | | | | | | |
| | | | | | | | | | | |
| 10/15/96 | 17:50 | BKG1015A | | Flowing N2 - Fairly wet | | | | | | |
| | | | | | | | | | | |
| | 17:50 | | | *Leak check (time = 0, P=4.1) at (time = 2, P=10.1) | | | | | | |
| | | | | | | | | | | |
| | 17:58 | CTS1015A | | Temp 123 C (cell) | | | | | | |
| | | | | | | | | | | |
| 10/16/96 | 9:07 | BKG1016A | 36 passes | | 100 | 2.0 | Ambient | 725.4 | | NB/med |
| | 9:15 | CTS1016A | 36 passes | Ethylene 99.4 ppm in N2 AAL16529 | 100 | 2.0 | Ambient | 725.4 | 1016A | NB/med |
| | 9:30 | CTS1016B | 36 passes | Ethylene 20 ppm in N2 Almo 29430 | 100 | 2.0 | Ambient | 725 | 1016A | NB/med |
| | 10:45 | BKG1016B | 36 passes | Background/N2 | 100 | 1.0 | 250F,121C | 726.9 | | |
| | 10:57 | CTS1016C | 36 passes | 20 ppm in N2 Almo 29430 | 50 | 1.0 | 250F,121C | 726.4 | | |
| | 11:11 | HCl001 | | HCl 103.0 ppm 1A7805 | 50 | 1.0 | 250F,121C | | | |
| | 11:42 | HCl00A | | N2 in cell after purge showing HCl traces remaining | 50 | 1.0 | 250F,121C | | | |
| | 13:18 | BKG1016C | 36 passes | | 200 | 1.0 | 122C | 725.3 | | NB/med |
| | | | | | | | | | | |
| 10/17/96 | 18:35 | BKG1017A | 36 passes | Background after cell alignment | 200 | 1.0 | 120C | 724.1 | | |
| | 18:58 | CTS1017A | 36 passes | 20 ppm Ethylene | 50 | 1.0 | 122C | 722.4 | A | |
| | 19:10 | BKG1017B | 36 passes | N2 dryer | 100 | 1.0 | 122C | 722.4 | | NB/med |
| | 19:21 | CTS1017B | 36 passes | 20 ppm | 50 | 1.0 | 122C | 722.4 | B | NB/med |
| | 20:00 | SF6EA001 | 36 passes | 4.01 ppm cyl #A7853 | 50 | 1.0 | 122C | 720.4 | B | |
| .10/18/96 | 9:47 | BKG1018A | 36 passes | | 100 | 1.0 | 121C | 716.8 | | NB/med |
| | 9:53 | CTS1018A | 36 passes | 20 ppm Ethylene | 50 | 1.0 | 121C | 716.8 | A | |
| | 10:03 | SF6EA002 | 36 passes | SF6 @ 4.01 ppm undiluted | 50 | 1.0 | 121C | 716.8 | A | |
| | 10:12 | HClEA001 | 36 passes | HCl 103.0 ppm undiluted (static in the cell) | 50 | | | | | |
| | 10:17 | HClEA002 | 36 passes | Same fill of HCl 5 minutes later | 50 | 1.0 | 121C | 716.8 | A | NB/med |
| | 10:27 | SF6HCl01 | | 50/50 mixture total flow = 48 through cell | 50 | 1.0 | 121C | 716.8 | A | NB/med |
| | 10:32 | SF6HCl02 | | Same fill static | | | | | | |
| | 10:42 | | | *leak check through back of cal manifold (time=0, P=6.3) at (time=1, P=14.0) | | | | | | |
| 10/18/96 | 13:45 | BKG1018B | 36 passes | | 100 | 1.0 | 122C | 715.7 | | NB/med |
| | 16:27 | BKG1018C | 36 passes | | 100 | 1.0 | 122C | 715.7 | | NB/med |
| | 16:33 | CTS1018B | 36 passes | | 50/100 | 1.0 | 122C | 715.7 | | C |
| | | | | | | | | | | |
| 10/19/96 | | | | *leak check cell (time=0, P=5.3torr), (time=2min, P=8.2torr), (time=0, P=798.8), (time=1, P=800.2) | | | | | | |
| | | | | | | | | | | |
| 10/19/96 | 9:32 | BKG1019A | 36 passes | Hydrator stack | 100 | 1.0 | 122C | 717.6torr | | NB/med |
| | 9:50 | CTS1019A | 36 passes | 20 ppm Ethylene | 50/100 | 1.0 | 122C | 717.6torr | A | |
| | 9:55 | CTS1019B | 36 passes | 20 ppm Ethylene 2nd fill | | | | | A | |
| 10/19/96 | 10:55 | BKG1019B | 16 passes | Shorter path length for 38% moisture. Using ZnSe Window | 100 | 1.0 | 122C | 717.9 | | NB/med |
| | 11:02 | CTS1019C | 16 passes | 20 ppm Ethylene | 50/100 | 1.0 | 122C | 717.5 | B | NB/med |
| | 11:13 | CTS1019D | 16 passes | 20 ppm Ethylene | 50/100 | 1.0 | 122C | 717.5 | B | NB/med |

Data Sheet: FTIR Background and Calibration Spectra: Eastern Ridge Lime Kiln. EPA Work Assignment 4-01.

| Date | Time | File Name | Path | Location/Notes | #scans | Res (cm-1) | Cell temp (F) | Pressure | BKG | Apod |
|---|---|---|---|---|---|---|---|---|---|---|
| | 11:28 | CTS1019E | 16 passes | 99.4 ppm Ethylene | 50/100 | 1.0 | 122C | 717.4 | B | NB/med |
| | 11:35 | CTS1019F | 16 passes | 99.4 ppm Ethylene | 50/100 | 1.0 | 122C | 717.5 | B | NB/med |
| | 11:41 | SF6HY001 | 16 passes | 4.01 ppm SF6 cal. standard | 50/100 | 1.0 | 122C | | B | NB/med |
| | | | | | | | | | | |
| 10/19/96 | 11:45 | SF6HY002 | 16 passes | Second sample SF6 4.01 ppm | 50/100 | 1.0 | 122F | 717 | B | NB/med |
| | 12:40 | BKG1019C | 16 passes | Closed down aperature to reduce energy | 100 | 1.0 | 122F | 717.4 | | |
| | 13:42 | CTS1019G | 16 passes | 99.4 ppm Ethylene | 50/100 | | 122F | 716.9 | C | NB/med |
| | 13:44 | CTS1019H | 16 passes | 99.4 ppm Ethylene | 50/100 | 1.0 | 122F | 716.9 | C | NB/med |
| | 14:06 | SF6HY003 | 16 passes | SF6 4.01 ppm | 50/100 | 1.0 | 122F | 716.5 | C | NB/med |
| | 14:10 | SF6HY004 | 16 passes | SF6 4.01 ppm | 50/100 | 1.0 | 122F | 716.4 | C | NB/med |
| | 16:09 | | | started spike (SF6) up to probe @ 1.00ppm total flow = 65 | | | | | | |
| | 16:14 | BKG1019C | 16 passes | N2 | 100 | 1.0 | 122C | 717.3 | | |
| | 16:20 | CTS1019I | 16 passes | 99.4 ppm Ethylene In Nitrogen | 50/100 | 1.0 | 122C | 717.3 | D | NB/med |
| | | | | | | | | | | |

Data Sheet: FTIR Batch Samples: Eastern Ridge Lime Kiln. EPA Work Assignment 4-01.

| Date | Sample time | File name | Path | Location/Notes | #scans | Res (cm-1) | Cell Temp (F) | Spk/Unsp | Sample Cond. | Sample Flow | BKG |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10/16/96 | 14:55-14:58 | Ambient 1 | 36 passes | Inlet probe | 50 | 1.0 | 123C | U | H/W | 110 | C |
| | 15:02-15:04 | SCINL001 | 36 passes | Inlet to scrubber | 50 | 1.0 | 123C | U | H/W | 110 | C |
| | 15:10-15:14 | SCINL002 | 36 passes | Inlet to scrubber | 50 | 1.0 | 123C | U | H/W (P=722.2) | 110 | C |
| | 15:15-15:21 | SCOUT001 | 36 passes | flow restricted at about 30 THC approx. 2 ppm | 50 | 1.0 | 123C | U | H/W | 110 | C |
| | 15:33-15:50 | SCOUT002 | 36 passes | flow restricted to about 10 | 50 | 1.0 | 123C | U | H/W | 110 | C |
| | | | | | | | | | | | |
| 10/18/96 | 10:44-10:46 | SCOUT201 | 36 passes | Scrubber outlet west (P=716.3) | | 1.0 | 122F | U | H/W | 85 | 1018A |
| | 10:48-10:50 | SCOUT202 | 36 passes | Scrubber outlet west (P=716.3) | | 1.0 | 122F | U | H/W | 85 | 1018A |
| | 10:52-10:54 | SCINL201 | 36 passes | Scrubber inlet | | | | U | | 120 | 1018A |
| | 10:57 | SCINL202 | 36 passes | Scrubber inlet | | | | U | | 120 | |
| | 11:02-11:04 | SCOUT203 | 36 passes | Scrubber outlet west | | | | U | | 80 | |
| | 11:06-11:07 | SCOUT204 | 36 passes | Scrubber outlet west | | | | U | | 75 | |
| | 11:10-11:11 | SCINL203 | 36 passes | Scrubber inlet | | | | U | | 120 | |
| | 11:13-11:15 | SCINL204 | 36 passes | Scrubber inlet | | | | U | | 120 | |
| | 11:17 | SCOUT205 | 36 passes | Scrubber outlet west | | | | U | | | |
| | | | | | | | | | | | |
| | 11:22 | | 36 passes | SF6 spike on to inlet | | | | U | | | |
| | 11:24 | SCOUT205 | 36 passes | Scrubber outlet west | | | | U | | | |
| | 11:29-11:31 | SCINS205 | 36 passes | spiked w/ 1.00lpm SF6 | | | | S(SF6) | | 120 total 1.00 spike | |
| | 11:34 | SCINS206 | 36 passes | spiked w/ 1.00lpm SF6 | | | | S(SF6) | | 120 total 1.00 spike | |
| 10/18/96 | 11:37-11:39 | SCINS207 | 36 passes | spiked w/SF6 at inlet | 50/100 | 1.0 | 122C | S(SF6) | H/W | total =120, SF6=0.98lm | A |
| | 11:44 | HCl spike on | 36 passes | HCl spike on to inlet, spike = 1.00 lpm, total flow=120 | | | | | | | |
| | | | | | | | | | | | |
| | 11:46-11:48 | SCOUC207 | 36 passes | Condenser Sample scrubber outlet west | 50/100 | | | | | | |
| | 11:53-11:55 | SCOUC208 | 36 passes | Condenser Sample scrubber outlet west | 50/100 | | | | | | |
| | 11:59-12:01 | SCINH208 | 36 passes | inlet spiked w/HCl @ 1.05lpm | 50/100 | | | S(HCl) | | total flow=120 | |
| | 12:05-12:12 | SCINH209 | 36 passes | inlet spiked w/HCl @ 1.04lpm flow through cell | 50/100 | | | S(HCl) | | total flow=120 | |
| | | | | | | | | | | | |
| | | | | evacuate cell | | | | | | | |
| | 12:14-12:23 | SCINH210 | | new fill w/HCl spike | 50 | 1.0 | 122C | S(HCl) | | total=120, HCl=1.00 | |
| | 12:25 | Empty 001 | | evacuated cell | 50/100 | 1.0 | 122C | vacuated cell | | | A |
| | 12:27 | Empty 002 | | | | | | | | | |
| | 12:30 | SCINH211 | | HCl spike to inlet P=724.4, flow through cell = 40, spike = 0.96 | | | | | | total=120 | |
| | 12:36-12:38 | SCOUC209 | | Condenser from outlet | | | | | | total outlet flow = 40 (bouncing) | |
| | 12:37 | | | spike off to inlet | | | | | | total inlet flow = 120 | |
| | 12:44-12:47 | SCOUT210 | | H/W from scrubber outlet west | | | | | | | |
| | 12:51 | SCOUT211 | | fill to 360 torr with outlet sample diluted with N2, fill to 720 torr with N2 | | | | | | | |
| | | | | | | | | | | | |
| | 12:55-12:58 | SCOUD212 | 36 passes | fill to 360 w/N2, fill to 720 w/outlet sample | 50/100 | 1.0 | 122C | U | diluted | total=35 | 1018A |
| | | | | | | | | | | | |
| | 13:03-13:04 | SCINL212 | 36 passes | untreated direct to cell | 80/100 | 1.0 | 122C | U | H/W | 120 | A |
| | 13:08-13:10 | SCINL213 | | | | | | | | | |
| | 13:13-13:15 | SCINC214 | 36 passes | Condenser sample scrubber inlet, flow through th | 50/100 | | | | | | A |
| | 13:18-13:22 | SCINC215 | 36 passes | Condenser sample scrubber inlet, flow through c | 50/100 | | | | | | A |
| | 13:25 | SCOUT213 | 36 passes | Scrubber outlet west | 50/100 | 1.0 | 122C | U | H/W | approx. 30 | A |

Data Sheet: FTIR Batch Samples: Eastern Ridge Lime Kiln. EPA Work Assignment 4-01.

| Date | Sample time | File name | Path | Location/Notes | #scans | Res (cm-1) | Cell Temp (F) | Spk/Unsp | Sample Cond. | Sample Flow | BKG |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 13:55-13:57 | SCINC216 | | Condenser sample from inlet | 50/100 | 1.0 | 122C | U | Cond. | total = 120 | B |
| | 13:30-14:00 | | | switch outlet probe to east stack and replaced glass wool plug to improve flow to manifold | | | | | | | |
| | 14:05-14:08 | SCOUT214 | | Scrubber outlet east stack | 50/100 | 1.0 | 122C | U | H/W | total = 75 | B |
| 10/18/96 | 14:11-14:14 | SCOUC215 | | Scrubber outlet east stack | | | | | Cond. | | B |
| | 14:18-14:21 | SCOUC216 | | Scrubber outlet east stack | | | | | Cond. | | B |
| | 14:26-14:30 | SCOUT217 | | Scrubber outlet east stack | | | | | H/W | | B |
| | 14:33-14:36 | CONBLNK1 | | nitrogen through the condenser | | | | | | | B |
| | 14:35 | | | Probe box back in operation | | | | | | | |
| | | | | | | | | | | | |
| | 14:40-14:43 | SCOUT218 | 36 passes | Scrubber outlet east stack | 50/100 | 1.0 | 122C | U | H/W | total = 60 | B |
| | 14:45-14:47 | SCOUC219 | | Scrubber outlet east stack | 50/100 | 1.0 | 122C | U | Cond. | total = 60 | B |
| | 14:49-14:52 | SCOUC220 | | Scrubber outlet east stack | 50/100 | 1.0 | 122C | U | Cond. | total = 60 | B |
| | 14:55-14:56 | SCINL217 | | Scrubber inlet | 50/100 | 1.0 | 122C | U | H/W | total = 60 | B |
| | 15:00-15:02 | SCOUD221 | | Outlet west to 360torr w/N2, to 720torr w/sample | 50/100 | 1.0 | 122C | U | Dil | 50 | B |
| | 15:05-15:06 | SCOUD222 | | Outlet west to 600 w/N2, to 720 w/sample | 50/100 | 1.0 | 122C | U | Dil | 50 | B |
| | 15:08-15:09 | SCIND218 | | to 360 w/N2, to 720 w/scrubber outlet | 50/100 | 1.0 | 122C | U | Dil | 120 | B |
| | 15:15-15:16 | SCOUD223 | | to 360 w/N2, to 720 w/scrubber outlet east | 50/100 | 1.0 | 122C | U | D | 50 | B |
| | 15:19-15:22 | SCOUC224 | | Outlet east condenser | 50/100 | 1.0 | 122C | U | Cond | 50 | B |
| | 15:25-15:26 | SCINL219 | | Inlet | 50/100 | 1.0 | 122C | U | H/W | 120 | B |
| | 15:29-15:31 | SCINC220 | | Inlet | 50/100 | 1.0 | 122C | U | Cond | 120 | B |
| | 15:35-15:37 | SCOUC225 | | Outlet east condenser | 50/100 | 1.0 | 122C | U | Cond | 50 | B |
| | 15:42-15:44 | SCOUT226 | | Outlet east condenser | 50/100 | 1.0 | 122C | U | H/W | 50 | B |
| | | | | | | | | | | | |
| 10/18/96 | 15:50-15:51 | SCIND221 | 36 passes | Inlet to 360 w/N2, to 720 w/sample | 50/100 | 1.0 | 122C | U | Dilute | 120 | B |
| | 15:55-15:57 | SCINL222 | 36 passes | Inlet untreated sample | 50/100 | 1.0 | 122C | U | H/W | 120 | B |
| | 15:58-15:59 | SCOUD227 | | to 67.5 w/sample, to 720 w/N2 | 50/100 | 1.0 | 122C | U | Dil | 50 | B |
| | 16:05-16:07 | SCOUC228 | | Outlet east condenser | 50/100 | 1.0 | 122C | U | Cond | 50 | B |
| | 16:10-16:12 | SCOUT229 | | Outlet east condenser | 50/100 | 1.0 | 122C | U | H/W | 50 | B |
| | | | | | | | | | | | |
| RATOR STACK | | | | Sample 1 line on manifold total flow=85 | | | | | | | |
| | | | | | | | | | | | |
| 10/19/96 | 12:06-12:08 | HYDHW001 | 16 passes | from hydrator stack, some water condensed in th | 50/100 | | | U | H/W | 70 in stack | B |
| | | | | | | | | | | | |
| | | | | | | | | | | | |
| | 12:14-12:15 | HYDCN002 | 16 passes | through condenser | 50/100 | 1.0 | 122F | U | Cond. | 70 | B |
| | 12:19-12:21 | HYDCN003 | 16 passes | through condenser | 50/100 | 1.0 | 122F | U | Cond. | 70 | B |
| | 12:27-12:28 | HYDDI004 | | diluted to 600 w/N2, to 718 w/sample | 50/100 | 1.0 | 122F | U | Dil | 70 | |
| | 12:43-12:44 | HYDDI005 | | diluted to 600 w/N2, to 718 w/sample | 50/100 | 1.0 | 122F | U | Dil | 60 | C |
| | 12:47-12:49 | HYDHW006 | | Hot wet | 50/100 | 1.0 | 122F | U | H/W | 60 | C |
| | 12:52-12:55 | HYDCN007 | | Condenser | 50/100 | 1.0 | 122F | U | Cond | 60 | C |
| | 12:59-13:01 | HYDHW008 | 16 passes | Hot wet | 50/100 | 1.0 | 122F | U | H/W | total = 60 | C |
| | 13:07-13:09 | HYDD1009 | 16 passes | dilution @ 2:1 to 360 w/N2, to 720 w/sample | 50/100 | 1.0 | 122F | U | H/W | total = 60 | C |
| | 13:12-13:14 | HYDD1010 | 16 passes | dilution @ 2:1 to 360 w/N2, to 720 w/sample | 50/100 | 1.0 | 122F | U | H/W | total = 60 | C |
| | 14:09 | | | Started SF6 spike up to probe @ 1.04 lpm, total flow =65 | | | | | | | |
| | 14:19-14:22 | HYDHS012 | 16 passes | Hot wet spiked w/SF6 | 50/100 | 1.0 | 122F | U | H/W | total = 60 | C |

Data Sheet: FTIR Batch Samples: Eastern Ridge Lime Kiln. EPA Work Assignment 4-01.

| Date | Sample time | File name | Path | Location/Notes | #scans | Res (cm-1) | Cell Temp (F) | Spk/Unsp | Sample Cond. | Sample Flow | BKG |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 14:27-14:28 | HYDHS013 | | Hot wet spiked w/SF6 0.98 lpm | 50/100 | 1.0 | 122F | U | H/W | total = 75 | |
| | 14:33-14:34 | HYDHS014 | | Hot wet spiked w/SF6 0.98 lpm | 50/100 | 1.0 | 122F | U | H/W | total = 75 | |
| | 14:36 | | | started HCl spike @ 1.00 lpm | | | | | | total flow =75 | |
| | 14:44-14:46 | HYDHS015 | | spiked w/HCl @ 0.97- 0.98 lpm, flow through at 717.3 torr | | | | | | total flow =75 | |
| | 14:49 | HYDHS016 | | spiked w/HCl @ 0.99 lpm, flow through at 719 torr | | | | | | total flow =78 | |
| | 14:56-14:59 | HYDHS017 | | spiked w/HCl @ 1.03 lpm, flow through at 719.2 torr | | | | | | total flow =78 | |
| 10/19/96 | | | | moisture condensing in rotameter cell | | | | | | | |
| | 15:05-15:10 | HYDHS018 | | spiked w/HCl @ 1.17 lpm, flow through cell at about 50, rotameter to cell is dry, manifold @ 320F, P=716.5 torr | | | | | | flow out vent = 25 | |
| | | | | continued purging cell as in HYDSO18 | | | | | | | |
| | 15:23 | HYDHS019 | 16 passes | continued purging cell, rotameter to cell still dry | | | | | | | |
| | | | | continued purge flow through @ about 50, P=711.8 torr | | | | | | | |
| | 15:31 | HYDHS020 | | spike flow = 1.06 lpm | | | | | | | |
| | | | | Moisture was @ 58% at Hydrator stack | | | | | | | |
| | | | | | | | | | | | |

Eastern Ridge

Data Sheet: FTIR CTS and Background Spectra. Lime Kilns. EPA W.A. 3804-01.

| Date | Time | File Name | Path M | Location/ Notes | # scans | Res. $cm^{-1}$ | Cell Temp. °F | Press. | BKG | Apod |
|---|---|---|---|---|---|---|---|---|---|---|
| 10/15/96 | 1700 | | | Leak check cell + Manifold under pressure 931 torr. Held steady for 1 minute | | | | | | |
| 10/15/96 | 1750 | BKG1015A | ? | flowing $N_2$ - fairly wet | | | | | | |
| | 1750 | | | leak check Time = 0 P = 4.1 Time = 2 P = 10.1 | | | | | | |
| | 1758 | CTS 1015A | | Temp 123°C (cell) | | | | | | |
| | | CTS 1015A | | | | | | | | |
| 10/16/96 | ~~9:02~~ | BKG 1016 A | ~20M | | 100 | 2 | Ambient | ~~730.8~~ 725.4 | | NB/med. |
| | ~~915~~ | CTS 1016A | " | Ethylene 99.4 ppm in $N_2$ AAL16529 | (100) | 2 | " | " | 1016A | " |
| | ~~[redacted]~~ | ~~[redacted]~~ | | | | | | | | |
| | 936 | CTS 1016 B | " | Ethylene 20 ppm in $N_2$ Alm029430 | 100 | 2 | " | 725.0 | " | " |
| | 1045 | BKG 1016B | " | Background $/N_2$ | 100 | 1 cm | 250F 121C | 726.9 | | |
| | 1057 | CTS 1016 C | " | 20 ppm in $N_2$ Alm0 29430 | 50 | " | " | 726.4 | | |
| | 11:11 | HCl 001 | | HCl 103.0 ppm 1H7805 | 50 | " | " | | | |
| | 11:42 | HCl 00 A | | $N_2$ in cell after Purge showing HCl traces remaining | 50 | " | " | | | |

Eastern Ridge

Data Sheet: FTIR CTS and Background Spectra. Lime Kilns. EPA W.A. 3804-01.

| Date | Time | File Name | Path M | Location/ Notes | # scans | Res. $cm^{-1}$ | Cell Temp. °F | Press. (torr) | BKG | Apod |
|---|---|---|---|---|---|---|---|---|---|---|
| 10/16/96 | 1318 | BKG1016C | 20M | | 200 | 1 $cm^{-1}$ | 122C | 725.3 | | NB/M |
| | | | | | | | | | | |
| 38 cell passes | | | | | | | | | | |
| 10/17/96 | 1835 | BKG1017A | 20M | Background after cell alignment | 200 | 1 $cm^{-1}$ | 120C | 729.1 | | NB/M |
| " | 1858 | CTS1017A | " | 20 ppm Ethylene | 50 | 1 $cm^{-1}$ | 122C | 722.4 | A | |
| | 1910 | BKG1017B | " | $N_2$ drier | 100 | " | " | " | | " |
| | 1921 | CTS1017B | " | 20 ppm | 50 | " | " | " | B | " |
| | 2000 | SF6EA001 | " | ~~Ethylene~~ 4.01 ppm cyl # A7853 | 50 | " | " | 720.4 | B | |
| | | | | | | | | | | |
| 10/18/96 | 9:47 | BKG1018A | 20M | | 100 | 1 $cm^{-1}$ | 121C | 718.8 | | NB/M |
| " | 9:53 | CTS1018A | 20M | 20 ppm Ethylene | 50 100 | " | " | " | A | " |
| | 10:03 | SF6Ea002 | " | SF6 @ 4.01 ppm undiluted. | 50 | " | " | " | A | " |
| | 10:12 | HClEa001 | " | HCl 1030 ppm undiluted Static 50 in cell | | | | | | |
| | 10:17 | HClEa002 | " | Same fill of HCl 5 minutes later | 50 | | | | | |
| | 10:27 | SF6HCl01 | | 50/50 mixture - total flow = 48 through cell. (static) | 50 | | | 716.9 | | |
| | | | | | | | | | | |
| | 10:32 | SF6HCl02 | | Same fill Static | | | | | | |
| | 10:42 | leak check | | through back of cal manifold | | | | | | |
| | | | | time = 0 P = 6.3 | | | | | | |
| | | | | time = 1 P = 14.0 | | | | | | |

Data Sheet: FTIR CTS and Background Spectra. Lime Kilns. EPA W.A. 3804-01.

| Date | Time | File Name | Path M | Location/ Notes | # scans | Res. $cm^{-1}$ | Cell Temp. °F | Press. | BKG | Apod |
|---|---|---|---|---|---|---|---|---|---|---|
| 10/18/96 | 1345 | BKG1018B | 36 passes | | 100 | 1 | 122C | 715.7 | | NB/mod |
| | 1627 | BKG1018C | " | | 100 | " | " | " | " | " |
| | 1633 | CTS1018B | " | | 50/100 | " | " | " | " | C |
| 10/19/96 | | leak check cell | | Time = 0 ; P = 5.3 torr<br>Time = 2 min; P = 8.2 "<br>Time = 0 ; P = 798.8<br>Time = 1 min ; P = 800.2 | | | | | | |
| 10/19/96 | 932 | BKG1019A | 36 passes | Hydrate stack | 100 | 1 cm-1 | 122C | 717.6 torr | | NB/mod |
| | 950 | CTS1019A | " | 20 ppm Ethylene | 50/100 | " | " | " | A | " |
| | 955 | CTS1019B | | " " " 2nd fill | | | | | A | |
| | | Reduced path length to 16 passes | | | | | | | | |
| | 1055 | BKG1019B | 16 passes | Shorten path length for 38% moisture. Using ZnSe Windows | 100 | 1 | 122C | 717.9 | | NB/mod |
| | 11:02 | CTS1019C | 16 passes | 20 ppm ethylene | 50/100 | 1 | 122C | 717.5 | B | NB/mod |
| | 11:13 | CTS1019D | " | " | " | " | " | " | " | " |
| | 11:28 | CTS1019E | " | 99.4 ppm Ethylene | " | " | " | 717.4 | B | " |
| | 11:35 | CTS1019F | " | " | " | " | " | 717.5 | " | " |
| | 11:41 | $SF_6$ Hy001 | " | 4.01 ppm $SF_6$ Cal standard | " | " | " | " | — | " |

Eastern Ridge

Data Sheet: FTIR CTS and Background Spectra. Lime Kilns. EPA W.A. 3804-01.

| Date | Time | File Name | Path M | Location/ Notes | # scans | Res. $cm^{-1}$ | Cell Temp. °F | Press. | BKG | Apod |
|---|---|---|---|---|---|---|---|---|---|---|
| 10/19/96 | 11:45 | SF6 Hy002 | 16 passes | Second Sample SF6 4.01 ppm | 50/100 | 1 | 122F | 717 | B | NB/mod |
| | 12:40 | BKG1019C | " | closed down aperture & reduced energy | 100 | 1 | 122F | 717.4 | | |
| | 13:42 | CTS1019G | " | 99.4 ppm Ethylene | 50/100 | 1 | 122F | 716.9 | C | NB/mod |
| | 13:49 | CTS1019H | " | " " | " | | | | | → |
| | 14:06 | SF6Hy003 | " | SF6 4.01 ppm | | | | 716.5 | | → |
| | 14:10 | SF6Hy004 | | | | | | 716.4 | | → |
| | 16:09 | Started | | Spike (>Fig) 4 to probe @ 1.000 lpm | | | total flow = | 65 | | |
| | 16:14 | BKG1019C | 16 passes | $N_2$ | 100 | 1 $cm^{-1}$ | 122C | 717.3 | | |
| | 16:20 | CTS1019I | | 99.4 ppm Ethylene in Nitrogen | 50/100 | 1 $cm^{-1}$ | " | " | D | NB/mod |

Eastern Ridge: ~~Inlet~~ Outlet of West Scrubber:

at start
Total flow inlet = 120 } probe out
" " outlet = 120

Data Sheet; FTIR Batch Samples; Lime Kilns, EPA WA, 3804-01.

| Date | Sample Time | File Name | Path M | Location/ Notes | # scans | Res. $cm^{-1}$ | Temp. °F | Spk/ Unspk | Sample Cond. | Sample Flow | BKG |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10/16/96 | 1455-1458 | Ambient 1 | 20 | Inlet probe | 50 | 1 cm⁻¹ | 123 C | U | H/W | 110 | C |
| " | 1502 1504 | scinl001 | " | Inlet to scrubber | " | " | " | U | H/W | " | C |
| | 1510-1514 | scinl002 | " | " | 50 | " | " | " | " P= 722.2 | " | " |
| | 1515-1521 | scoutl001 | " | Flow restricted about 30 THC ~ 2ppm | 50 | " | " | " | " | " | " |
| | 1533 1550 | scoutl002 | " | Flow restricted to about 10 | 50 | " | " | " | " | " | " |
| | | | | | | | | | | | |
| 10/18/96 | 1044-1046 | Scout201 | 20M | scrubber outlet West. P= 716.3 | | 1 cm⁻¹ | 122F | U | H/W | 85 | 1981 |
| " | 1048-1050 | scout 202 | " | " | | | | | | | " |
| | 1052-1054 | scinl201 | | Scrubber inlet | | | | U | | 120 | " |
| | 1057- | scinl 202 | | " | | | | | | " | |
| | 1102-1104 | scout 203 | | scrubber outlet West | | | | | | 80 | |
| | 1106-1107 | scout 204 | | " | | | | | | 75 | |
| | 1110-1111 | scinl 203 | | Scrubber inlet | | | | | | 120 | |
| | 1113-1115 | scinl 204 | | " | | | | | | 120 | |
| | 1117- | Scout 205 | | scrubber outlet west | | | | | | | |
| | | | | | | | | | | | |
| | 1122 | SF6 spike on | | to inlet | | | | | | (120 total 1.00 spike | |
| | 1124- | Scout 206 | | Scrubber outlet West | | | | | | | |
| | 1129-1131 | Scinl 205 | | Spiked w/ 1.00 lpm $SF_6$ | | | | S ($SF_6$) | | | |
| | 1134- | Scinl 206 | " | " " | | | | S " | | " | |

flowmeter
20 = ~0.0

Data Sheet: FTIR Batch Samples: Lime Kilns. EPA WA. 3804-01.

| Date | Sample Time | File Name | Path M | Location/ Notes | # scans | Res. $cm^{-1}$ | Temp. °F | Spk/ Unsp | Sample Cond. | Sample Flow | BKG |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10/18/96 | 1137-1139 | Scm S207 | 20 | Spiked w/ $SF_6$ at inlet | 50/100 | 1cm | 122C | S($SF_6$) | H/w | total = 120 $SF_6$ = 1 0.98lpm | A |
| | 1144 | HCl spiked to inlet | | HCl spike on to outlet | | spike = 1.00 lpm | | | | | |
| | | | | | | total flow = 120 | | | | | |
| | 1146-1148 | SCOUC 207 ~~Scat Bott~~ | | Condenser Sample scrubber outlet west | 50/100 | | | | | | |
| | 1153-1155 | SCOUC 208 | | " | " | | | | | | |
| | | | | | | | | | | | |
| | 1159-1201 | SCIN H208 | | inlet spiked w/ HCl @ 1.05 lpm | | | | | | total flow = 120 | |
| | 1205-1212 | SCIN H209 | | " " HCl @ 1.04 lpm | | flow through cell at 40 | | | | | |
| | | | | Cell P = 719.1 | | (total flow = 120 minus through cell = 80) | | | | | |
| | | evacuate cell | | | | | | | | | |
| | 1214-1223 | Scm H210 | | new fill w/ HCl spike | 50 | 1 | 122C | S(HCl) | | total = 120 HCl = 1.00 | |
| | ~~12:24~~ | ~~Scat H211~~ | | | | | | | | | |
| | 12:25 | Empty 001 | | evacuated Cell | 50/100 | 1 | " | evacuated cell | | | A |
| | 12:27 | Empty 002 | | | | | | | | | |
| pumped out sample cell empty | 1230 | scm H211 | | HCl spike to inlet P = 724.4 | | | flow through cell = 40 | | | total flow = 120 Spike = 0.98 | |
| | | | | | | | | | | | |
| | 1236-1238 | SCOUC 209 | | Condenser from outlet. | | | | | | total outlet flow = 40 (bouncing) | |
| | 1237 | Spike off to inlet | | | | | | | | total inlet flow = 120 | |
| | 1244-1247 | S Cont 210 | | H/w from scrubber outlet west. | | | | | | total = 40 | |
| | 1251- | S Cont 211 | | fill to 360 Torr with outlet sample | diluted w/ $N_2$ | | | | | | |

f20 to 720 torr w/ $N_2$

Data Sheet: FTIR Batch Samples: Lime Kilns, EPA WA, 3804-01.

| Date | Sample Time | File Name | Path M | Location/ Notes | # scans | Res. $cm^{-1}$ | Temp. °F | Spk/ Unsp | Sample Cond. | Sample Flow | BKG |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10/18/10 | 1255-1258 | SCOUD212 | 20m | fill to 360 w $N_2$ | 50/100 | 1cm$^{-1}$ | 122C | U | Dilute | total ~35 | 10 A |
| | | | | fill to 720 w outlet Sample | | | | | | | |
| | 1303-1304 | SCMC212 | 3m | untreated liquid to cell | 80/100 | " | " | " | H/w | 120 | A |
| | 1308-1310 | SCIC213 | | | | | | | | | |
| | 1313-1314 | SCMC214 | " | Condenser Sample scrubber inlet | 5%100 | | flow through Condenser = 20 | | | | A |
| | 1318-1322 | SCMC215 | " | " | " | | | " | | | A |
| | 1325- | SCOUT213 | " | scrubber outlet west | " | 1cm$^{-1}$ | 122C | U | H/w | ~30 | A |
| | | | | Press 682 total flow dropped to 0 probably pulled in some ambient air | | | | | | | |
| | 1348-1351 | ~~SCMC215~~ Condenser | | | | | | | | | B |
| | 1355-1357 | SCMC216 | | Condenser sample from inlet | 96/100 | 1 | 122C | U | Cond. | 120-20 total to Cond | B |
| | 1330-1400 | Switch outlet probe to East stack and replaced glass wool plug to improve flow to manifold. | | | | | | | | | |
| | 1405-1408 | SCOUT214 | | Scrubber outlet East stack | 50/100 | 1 | 122C | U | H/w | 75 total | B |
| | 1411-1414 | SCOUC215 | | " | | | | | Cond. | | B |
| | 1418-1421 | SCOUC216 | | " | | | | | Cond | | |
| | 1426-1430 | SCOUT217 | | scrubber outlet east stack | | | | | H/w | | |
| | 1433-1436 | CAL BLK | | nitrogen through the Condenser | | | | | | | |

1435 Probe box Back in operation.

Probe Box blown out

Check flow meter @ 0 = -0.07

Data Sheet: FTIR Batch Samples: Lime Kilns, EPA WA, 3804-01.

| Date | Sample Time | File Name | Path M | Location/ Notes | # scans | Res. $cm^{-1}$ | Temp. °F | Spk/ Unsp | Sample Cond. | Sample Flow | BKG |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10/18/96 | 1440-1443 | ~~Scout~~ Scout 218 | 360 pass | Scrubber outlet East stack | 50/100 | 1 | 122C | U | H/w | Total-60 | B |
| | 1446-1447 | SCOUC219 | | " " | | | | → | Cnd | | → |
| | 1449-1452 | SCOUC220 | | " " | | | | → | Cond | | → |
| | 1455-1456 | Scind 217 | | Scrubber Inlet | | | | → | H/w | | → |
| | 1500-1502 | SCOUD221 | | outlet west to 360 ton w/ $N_2$ to 720 ton w/ sample | | | → | | Dil | 60 | ↓ |
| | 1505-1506 | SCOUD222 | | outlet West to 600 w/ $N_2$ to 720 w/ sample | | | | → | Dil | 60 | ↓ |
| | 1508-1509 | SCm 0218 | | to 360 w/ $N_2$ to 720 w/ Scrubber outlet | | | | → | Dil | 120 | B |
| | 1515-1516 | SCOUD223 | | to 360 w/ $N_2$ to 720 w Scrubber outlet East | | | | → | D | 50 | B |
| | 1519-1520 | SCOUC224 | | outlet East Condenser | | | | → | H/Cnd | 50 | B |
| | 1525-1526 | scind 219 | | Inlet | | | | → | H/w | 120 | B |
| | 1529-1531 | Scm C220 | | Inlet | | | → | | Cnd | 120 | B |
| | 1535-1537 | SCOUC225 | | outlet East Condenser | | | | → | Cnd | 50 | B |
| | 1542-1544 | SCOUT 226 | | outlet " " | | | | → | H/w | 50 | B |

Ambient Pressure :

Data Sheet: FTIR Batch Samples: Lime Kilns, EPA WA, 3804-01.

| Date | Sample Time | File Name | Path M | Location/ Notes | # scans | Res. $cm^{-1}$ | Temp. °F | Spk/ Unsp | Sample Cond. | Sample Flow | BKG |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10/18/96 | 1540-1551 | SCM0221 | 36 p | inlet to 360 w/$N_2$ to 720 w/sample | 50/100 | \ | 122C | U | Dilute | 120 | B |
| | 1556-1557 | SCMR222 | " | inlet untreated Sample. | | | | | H/W | 120 | B |
| | 1558-1559 | SCOUD 227 | | to 67.5 w/Sample to 120 w/$N_2$ | | | | | Dil | 50 | B |
| | 1605-1607 | SCOUC228 | | outlet East Condenser | | | | | Cond | 50 | B |
| | 1608-1612 | SCOUT229 | | " " H/W | | | | | H/W | 50 | B |
| Hydrator | | Stack | | "Sample 1" Line on manifold. | | | | | Total flow = 85 | | |
| 10/19/96 | 1206-1208 | HydHW001 | 16 passes | from hydrator stack | 50/100 | | | U | H/W | 70 in stack | B |
| | | | | Some water Condensed in the manifold flow meter to cell - pumped out through rotameter to cell. | | | | | Manifold @ 310 F. | | |
| | 1214-1215 | HydCN002 | " | through Condenser | 50/100 | 1 | 122F | U | Cond. | 70 | B |
| | 1219-1221 | HydCN003 | " | " | 50/100 | | | U | " | 70 | B |
| 1227-1228 | [illegible] | HydDi004 | | Diluted to 600 w/$N_2$ to 718 w/sample | | | | | Dil | " | |
| | 1243-1244 | HydDi005 | | " | | | | | Dil | 60 | C |
| | 1247-1249 | HydHW006 | | Hot wet | | | | | H/W | 60 | C |
| | 1252-1255 | HydCN007 | | Condenser | | | | | Cond | " | C |

Data Sheet: FTIR Batch Samples: Lime Kilns. EPA WA. 3804-01.

| Date | Sample Time | File Name | Path M | Location/ Notes | # scans | Res. $cm^{-1}$ | Temp. °F | Spk/ Unsp | Sample Cond. | Sample Flow | BKG |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10/14/96 | 1259-1301 | HyD HW008 | 16 passes | Hot wet | 50/100 | 1 | 122F | U | H/W | total = 60 | C |
| | 1307-1309 | HYPD1009 | " | Dilut in @ 2:1 to 360 w/N2 to 720 w/sample 50/100 | 1 | " | " | " | " | C |
| | 1312-1314 | HyDD1010 | " | " " | | | | | | → |
| | 1330- | Hyd H0011 | 16 pass | Hot/wet Must not have done this one. DB: Not on Disk | | | | | | |
| | 14:04 | started | | $SF_6$ spike up to Probe @ 1.04 lpm | | | | | total flow = 65 | |
| | 1419-1421 | Hyd HS012 | " | Hot/wet spiked w/ $SF_6$ | | | | | | C |
| | 1427-1429 | Hyd HS013 | | " " 0.98 lpm | | | | | total flow = 75 | |
| | 1433-1434 | Hyd HS014 | | " " 0.98 lpm - 0.97 | | | | | " = 75 | |
| | 1436 | started | | HCl Spike @ 1.00 lpm | | | | | total flow = 75 | |
| | 1444-1446 | Hyd HS015 | | spiked with HCl @ 0.97 - 0.98 lpm | | | | flow through @ 717.3 torr | total flow = 75 | |
| | 1449 | Hyd HS016 | | " " @ 0.98 lpm | | | | flow through @ 719 | total flow = 78 | |
| | | | | moisture condensing in Rotameter to cell | | | | | | |
| | 1456-1458 | Hyd HS017 | | spiked w/ HCl @ 1.03 lpm | | | | flow through @ 719.2 torr | total flow = 78 | |
| | 1505-1510 | Hyd HS018 | | " " " 1.17 lpm | | | | flow through cell @ about 50 | | |
| | | | | manifold @ 320 F | | | | flow out end = 25 | | |

↳ rotameter to cell is dry. 716.5 torr.

Data Sheet: FTIR Batch Samples; Lime Kilns, EPA WA. 3804-01.

| Date | Sample Time | File Name | Path M | Location/ Notes | # scans | Res. $cm^{-1}$ | Temp. °F | Spk/ Unsp | Sample Cond. | Sample Flow | BKG |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10/19/06 | | | | Continued purging cell as in Hyd S018 | | | | | | | |
| | Spectrum Time | under continuous purge. | | | | | | | | | |
| | | | | | | | | | | | |
| | 1523 | Hyd HS019 | 16 pass | " Rotameter to cell still dry. | | | | | | | |
| | | | | Continued purge flow through @ about | | | ↳ | 111.8 lpm | | | |
| | 1531 | Hyd HS020 | | Spike flow = 1.06 lpm | | | | 50 | n (5 lpm) | | |

Moisture was @ 58% at Hydrator stack

# APPENDIX C.

# FTIR ANALYTICAL RESULTS

**Draft Report**

**December 1996**

# Results of Least Squares Concentration Determinations for FTIR Spectra Collected at Eastern Ridge Lime Kiln

Prepared by:

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Prepared for:

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## Disclaimer

This document was prepared by Rho Squared under Midwest Research Institute Purchase Order Number D02329. This document has been reviewed neither by Midwest Research Institute nor by the U. S. Environmental Protection Agency.

The opinions, conclusions, and recommendations expressed herein are those of the author, and do not necessarily represent those of Midwest Research Institute or those of the United States Environmental Protection Agency.

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Data Collection and Analytical Method

Midwest Research Institute performed extractive FTIR source testing in October 1996 at Eastern Ridge lime kiln and provided the spectral data to Rho Squared for preliminary quantitative least squares analysis. Compounds of quantitative interest in the samples, referred to below as analytes and identified in conversations with Dr. Tom Geyer of MRI, are HCl, $H_2CO$, CO, $SO_2$, NO, and $NO_2$. The spectra also contain features from the interferant compound $H_2O$, and $SF_6$ was quantified in some spectra as the diluent tracer compound used for dynamic spiking.

References 1 through 5 comprise a thorough description of one technique for analyzing FTIR absorbance spectra. Using the programming language ARRAY BASIC™ (GRAMS,™ Version 3.02, Galactic Industries Corporation, Salem, New Hampshire) Rho Squared has prepared a computer program to perform this technique. The "classical least squares" (CLS) or "K-Matrix" technique and the associated computer program are described in Reference 6. The terminology and basic analytical approach employed in this work are described in the "EPA FTIR Protocol" (Reference 7).

The program allows the analyst to select a number of analytical regions and to specify which of the selected reference spectra will be employed in determining the corresponding compound concentrations. Baseline parameters (linear, and quadratic in some cases) were also determined in the calculations but are not reported here. Reference spectra for the current work were provided by MRI or were taken from the EPA FTIR spectral library of Hazardous Air Pollutants (hereafter, the "EPA library"). Additional information regarding the reference spectra is listed below.

The program calculates the standard $1\sigma$ uncertainty in each concentration. However, all uncertainties quoted below are equal to four times the calculated $1\sigma$ values. The program also calculates the residual spectra (the difference between the observed and least squares fit absorbance values) for each sample spectrum and analytical region. These data are not presented

here but have been submitted to MRI in digital form with this report. The GRAMS™ format residual spectral files have DOS extensions of the form "*rn*", where the integer *n* designates the analytical region label for a particular analytical run. Although this labeling scheme does not uniquely identify the residual spectra, the frequency ranges are unique and make identification of the various spectra straightforward.

For each analytical region, compounds whose reference spectra are employed in the least squares fits are characterized either as analytes or as interferants. Table 1 lists the analytical regions and summarizes the characterizations of the six target compounds (HCl, $H_2CO$, CO, $SO_2$, NO, and $NO_2$). Note that each target compound appears as an analyte in one and only one analytical region. The concentrations and uncertainties reported in this work correspond to the analyte characterizations of Table 1.

TABLE 1. ANALYTICAL REGIONS AND COMPOUND CHARACTERIZATIONS[a,b]

| Analytical Region | Lower Bound ($cm^{-1}$) | Upper Bound ($cm^{-1}$) | HCl | $H_2CO$ | CO | $SO_2$ | NO | $NO_2$ | $H_2O$ | $CO_2$ | $SF_6$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 900 | 1200 | - | - | - | A | - | - | I | I | A |
| 1 | 1581.7 | 1613.3 | | | | | | A | I | - | - |
| 2 | 1898.6 | 1904.8 | - | - | - | - | A | - | I | - | - |
| 3 | 2110 | 2125.5 | - | - | A | - | - | - | - | I | - |
| 4 | 2747 | 2848 | A | A | - | - | - | - | - | - | - |

[a]I indicates "interferant," A indicates "analyte," and the hyphen indicates that the compound was not included in the least squares spectral analyses of the analytical region.
[b]Baseline slope and offset for each analytical region were also determined in the least squares concentration analyses (see Reference 6). Quadratic baseline contributions were also determined for region 4.

MRI provided a total of 87 spectral files for analysis. After determining concentration values and uncertainties for each compound in each analytical region of every sample spectrum, the program rejects compounds from each analytical region if either a) the determined concentration is negative or b) the $4\sigma$ uncertainty in the concentration is greater than the (positive) determined concentration. If a compound is rejected from a region for a particular spectrum, the concentration is recorded as exactly zero in the output file along with the related uncertainty from the original fit. Such uncertainty values are extremely conservative upper limits

on the uncertainty of the reported zero concentration values. Concentration results and their 4σ uncertainties were recorded in Excel™ spreadsheet files and provided to MRI for inclusion in a comprehensive report to EPA.

Pathlength Determinations

Absorption pathlengths were determined from the field test CTS spectra and EPA library CTS spectra of ethylene ($C_2H_4$) . For high temperature spectra, the EPA library interferograms cts0115a.aif and bkg0115a.aif were de-resolved to the appropriate spectral resolution (either 1 or 2 $cm^{-1}$) according to the procedures of reference 7 (Appendix K). The same procedure was used to generate low-temperature spectra from the original interferometric data in the EPA library files cts0829a.aif and bkg0829a.aif. The resulting files were used in least squares fits to the appropriate field CTS spectra (see reference 7, Appendix H) in two regions (the FP, or "fingerprint" region from 790 to 1139 $cm^{-1}$ and the CH, or "CH-stretch region" from 2,760 to 3,326 $cm^{-1}$). The fit results for each region, test, and set of test sampling conditions were averaged. They and their average uncertainties are presented in Tables 2 and 3. The CH values were used in analytical region 4; the FP values were used in all other analytical regions.

TABLE 2. PATHLENGTH DETERMINATION RESULTS FOR EASTERN RIDGE TEST DATA

| CTS Conditions | | CH region | | FP region | |
|---|---|---|---|---|---|
| # Passes | Temp (K) | Result (m) | % uncert. | Result (m) | % uncert. |
| 16 | 393 | 6.1 | 2.8 | 7.3 | 1.4 |
| 36 | 393 | 18.9 | 2.4 | 21.2 | 1.5 |

TABLE 3. REFERENCE SPECTRA

| | Analytical region | | | | |
|---|---|---|---|---|---|
| Compound | 0 | 1 | 2 | 3 | 4 |
| HCl | - | | | - | 097.alf |
| $H_2CO$ | - | | | | 087c1asb.spc [b] |
| CO | - | - | - | co20829a.spc | - |
| $SO_2$ | 198.alf | - | - | - | - |
| NO | - | - | 199c1bsa.spc | - | - |
| $NO_2$ | - | 200c1bse.spc | - | - | - |
| $H_2O$ | 194jsub.spc | 194fsub.spc | 194fsub.spc | - | - |
| $CO_2$ | 193c1bsa.spc | | | 193c1bsa.spc | - |
| $SF_6$ | (a) | - | - | - | - |

[a]File sf640p_1.alf was used for spectra recorded at (nominal) forty passes in the infrared absorption cell and for all Eastern Ridge data.
[b]Results of analyses excluding $H_2CO$ from this analytical region were also supplied to MRI.

## Reference Spectra

Reference spectra for the current work were provided by MRI or were taken from the EPA library. Table 4 lists the spectra used in the analyses for each analytical region.

TABLE 4. FRACTIONAL CALIBRATION UNCERTAINTY (FCU)

| Compound | FCU (%) |
|---|---|
| $SO_2$ | 4.6 |
| HCl | 8.5 |
| $SF_6$ (20 passes) | 1.5 |
| $SF_6$ (40 passes) | 1.2 |

For the compound HCl, the FTIR library spectra were de-resolved to 1 $cm^{-1}$ and normalized for absolute temperature, concentration, and absorption pathlength. The resulting files were averaged to provide a "reduced absorptivity" (see Reference 6), which was stored in the spectral file 097.alf and employed in all subsequent HCl analyses. The HCl analysis was applied to the de-resolved EPA library HCl spectra to determine the fractional calibration uncertainty (FCU), which is presented in Table 5. Similar procedures were followed to determine the reduced absorptivity and FCU values for the compounds $SO_2$ and $SF_6$. For $SO_2$, 1.0 cm-1 resolution spectra provided by MRI were used; the spectra used for $SF_6$ were those recorded on the field instrument, at two different absorption pathlengths.

References


1. D.M. Haaland and R.G. Easterling, "Improved Sensitivity of Infrared Spectroscopy by the Application of Least Squares Methods," Appl. Spectrosc. 34(5):539-548 (1980).

2. D.M. Haaland and R.G. Easterling, "Application of New Least-Squares Methods for the Quantitative Infrared Analysis of Multicomponent Samples," Appl. Spectrosc. 36(6):665-673 (1982).

3. D.M. Haaland, R.G. Easterling and D.A. Vopicka, "Multivariate Least-Squares Methods Applied to the Quantitative Spectral Analysis of Multicomponent Samples," Appl. Spectrosc. 39(1):73-84 (1985).

4. W.C. Hamilton, Statistics in Physical Science, Ronald Press Co., New York, 1964, Chapter 4.

5. P.R. Griffiths and J.A. DeHaseth, Fourier Transform Infrared Spectroscopy, John Wiley and Sons, New York, 1986, ISBN 0-471-09902-3.

6. G. M. Plummer and W. K. Reagen, "An Examination of a Least Squares Fit FTIR Spectral Analysis Method," Air and Waste Management Association, Paper Number 96-WA65.03.

7. "Protocol for the Use of Extractive Fourier Transform Infrared Spectrometry for the Analyses of Gaseous Emissions from Stationary Sources, " U.S. Environmental Protection Agency (EMTIC Bulletin Board, 1995).

# APPENDIX D.

# PROCESS DESCRIPTION AND DATA

RESEARCH TRIANGLE INSTITUTE

Center for Environmental Analysis

**MEMORANDUM**

TO: Joseph Wood, ESD/MICG (MD-13)
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

FROM: Cybele Brockmann, RTI

DATE: July 31, 1997

SUBJECT: Process Description for Eastern Ridge Lime

REFERENCE: Information Gathering and Analysis for the Lime Manufacturing Industry NESHAP
EPA Contract 68-D1-0118
ESD Project 95/06
RTI Project 6750-017

Attached is the description of processes at Eastern Ridge; processes were monitored during testing at the plant October 16-19, 1997.

3040 Cornwallis Road • Post Office Box 12194 • Research Triangle Park, North Carolina 27709-2194 USA
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## I. Process Description for Eastern Ridge Plant

Lime (CaO) is typically produced in the U.S. by crushing and then heating limestone ($CaCO_3$) in an inclined, rotating kiln. The limestone is heated to temperatures of around 2000 degrees Fahrenheit (deg F) which cause it to breakdown chemically into lime and $CO_2$. At Eastern Ridge, most of the lime is sold as CaO; a small amount (ten percent of production) is converted into hydrated lime ($Ca(OH)_2$.[1]

Limestone at the Eastern Ridge plant is surface-mined from a quarry located at the plant. The quarried limestone is crushed and screened into several sizes and then transferred to a storage area. Prior to entering the kiln, the sized stone is washed with water to remove dirt.

The number two kiln is an inclined rotating kiln with a design capacity of 350 tons of lime per day (115,150 tons per year).[2] The kiln is 392 feet long with a tapered diameter (11 feet in diameter at the front end of the kiln and 10 feet in diameter the remaining length of the kiln).[3] The incline of the kiln is 1/2 inch per foot.[4] Limestone enters the kiln at its back end (the highest point of incline) and tumbles through the kiln via gravity and the rotating motion of the kiln (typical rotating rates are 55 to 65 revolutions per hour). The residence time of the feed material in the kiln is four hours. Approximately two tons of limestone are required to produce a ton of lime.[5]

The combustion of fuel, which consists of pulverized coal suspended in air, occurs at the front end of the kiln (the origin and chemical composition of the coal at the time of testing are unknown). The coal is pulverized to the consistency of powder in a bowl mill (the bowl mill is exclusive to the number two kiln). Air from the firing hood, located directly above the combustion end of the kiln, is pulled into the bowl mill. The air preheats and dries the coal. A fan on the mill blows the air and dry pulverized coal from the mill into the kiln. Typically a quarter to a third of a ton of coal is consumed per ton of lime.[6]

As the lime exits the kiln, it drops into one of ten satellite coolers that are attached to the exterior of the kiln. The coolers are long cylindrical tubes (30 feet long by 8 feet wide in diameter) filled with chains. As the coolers rotate with the kiln, the lime tumbles through the chains which conduct heat away from the lime.[7] Lime drops from the cooler tubes onto a conveyor belt. The lime is conveyed to a screen, separated by particle size, and stored. Fines from product screening are collected, stored, and used in hydrate production.

Approximately ten percent of the lime produced at Eastern Ridge is chemically reacted with water to form a hydrated product.[8] The chemical reaction for hydration is as follows:

$$CaO + H_2O = Ca(OH)_2 + heat$$

Lime Hydrate

At Eastern Ridge, the hydration process is carried out in seven steps. In step one, lime fines are mixed with water in a pug mill to form a partially hydrated product. The pug mill is a horizontal cylinder that contains a shaft fitted with short, heavy paddles that push and mix the materials through the mill. The source of water to the pug mill is effluent from the wet scrubber that treats exhaust from steps two through seven (the scrubber is discussed further under Hydrator Emissions Control).[9] In steps two through seven, the partially hydrated product passes through a series of six mixing barrels which allow the mixture to fully react (the transfer time through all six mixing barrels is approximately thirty minutes). After the lime is hydrated, it is transferred to a storage bin, milled, and separated from impurities (such as unreacted lime and limestone) with a whizzer separator (similar to a cylone). Approximately 28,000 tons of hydrate are typically produced annually.[10]

## II. Emissions Control

### Kiln Emissions Control

Exhaust from the number two kiln is routed to two, parallel spray towers. The spray towers/scrubbers were manufactured by Ducon and were installed at the plant in the 1970's. Each scrubber is equipped with a fan which draws the kiln exhaust up through the tower. Water is sprayed into the tower at various points upstream of the fan and into the fan itself.[11] The exhaust from the fan exits through a stack. Effluent from the scrubbers is directed to a series of four settling ponds where solids are removed. Clarified water is recycled back to the scrubbers.

### Hydrator Emissions Control

The hydration process is exothermic, and part of the water in the hydrate mixture is vaporized. Gases from the hydrator, containing water and lime particles, are pulled by fan to a Ducon scrubber, scrubbed with 10 gallons per minute (gpm) of water (typical), and then vented to the atmosphere.[12] (The flow rate of scrubbing water varies somewhat with the moisture content of

the lime fines in step one of the hydration process. For example, newly processed lime fines have less moisture than fines which have been kept in storage; thus, the former may require more than 10 gpm while the latter may require less than 10 gpm.)[13] Effluent from the scrubber is added to the lime fines in step one. The Ducon scrubber is the same type of spray tower used to control the kiln exhaust.

Refer to Figure 1 for a diagram of the kiln, hydrator and associated emissions control. The diagram indicates the relative locations for each unit operation, direction of flow for material and gas, input and output of materials and gas, and approximate locations where process parameters were measured.

## III. Process Operation

Data indicating the operation of the kiln, the scrubbers treating the kiln exhaust, and the scrubber treating the hydrator exhaust are presented in this section. All process data for the kiln were manually recorded by RTI every 15 minutes during the emissions testing and taken from computer screens in the kiln control room; the recorded data were measured with instruments already in place and used by the plant for process control of the kiln.

For the scrubbers treating the kiln exhaust, PES measured the pressure drop across each of the scrubbers and measured/calculated the volumetric flow rates of water entering and exiting each of the scrubbers. To measure pressure drop, PES drilled pressure taps upstream of each scrubber tower and at the end of each exhaust stack. The pressure drop across the upstream tap and exhaust tap of each scrubber was measured using a U-tube manometer. The pressure drop across each scrubber was measured and recorded once during each run, just prior to testing.

PES measured the volumetric flow rate of water exiting the bottom of the each scrubber by placing a container of known volume below the water outlet and recording the time to fill the container. The opening of the container was slightly smaller than the water outlet, thus, the container only collected approximately 80 percent of the exiting water. PES took two measurements of the water flow rate exiting the bottom of each scrubber; the measurements were taken back-to-back during run 2 of the kiln 2 scrubber tests.

PES measured the temperature, gas flow, and moisture content of the kiln exhaust just prior to each scrubber tower and exiting each scrubber stack; based on these measurements, PES calculated

the volumetric flow rates of water vapor entering and exiting each scrubber. These calculated flow rates, along with the measured flow rate of water exiting each scrubber, were entered into a mass balance of water across the system to calculate the flow rate of water injected into each scrubber (see Figure 2 for a mass balance of water of the scrubber system).

During emissions testing, RTI manually recorded the water flow rate to the scrubber treating the hydrator. The water flow rate was measured by an instrument already in place and used by the plant for control of the hydrator. The water flow rate was initially recorded every 15 minutes; however, after no change was noted during the first hour, and after the operator of the hydrator stated that the flow rate would remain fairly constant, the readings were recorded less frequently.

Table 1 is a statistical summary of the process data collected during testing. Tables 2a, 2b, and 2c display all of process data collected during testing.

Table 3 is a comparison of the values of the process parameters recorded during testing to previously cited values of these parameters. Previously cited values were extracted from emission test reports provided by the plant (private testing was comissioned in 1989 and 1995);[14] a trip survey of the plant written by Research Triangle Institute in 1995;[15] a questionnaire filled out by the plant for EPA in 1995;[16] and standard operating procedures (SOP) of Eastern Ridge Lime plant.[17] Values cited by the kiln operator during testing are also included in Table 3.

Notes Pertaining to Test Data

Coal feed rate, limestone feed rate, kiln speed

Table 4 compares calculated coal feed rates with the average coal feed rates recorded during testing. Coal feed rates were calculated using previously cited values for tons of coal per ton of lime and tons of lime per ton of limestone and using the average limestone rates recorded during testing. Using the questionnaire values for tons of coal per ton of lime and tons of lime per ton of limestone, the calculated coal feed rates were 1.85, 2.06, and 1.89 tons of coal per hour. Using the value for tons of coal per ton of lime cited by the kiln operator and the 1995 test data, and using the questionnaire value for tons of lime per ton of limestone, the calculated coal feed rates were 4.36, 4.46, and 4.87 tons of coal per hour. The recorded average coal feed rates were 3.69, 3.65 and 3.61 tons of coal per hour (Table 4).

Front end temperature, back end temperature, excess air

As shown in Table 3, the average back end temperatures during testing were below both ranges of temperature specified in the SOP. The front end temperature fell within the operating range specified by the SOP. The percentage of oxygen in the kiln exhaust exceeded the SOP ranges on two of the test days.

Despite the fact that the back end temperature and the oxygen level were not within the ranges specified by the SOP, all of the kiln operators stated that they were operating the kiln under normal conditions during testing. They also stated that the operation of the kiln varies on a day to day basis depending on the weather, the size of the limestone, the moisture content of the coal, the BTU value of the coal, and other factors. These factors may explain why the average oxygen content in the kiln exhaust varied between days 10/17 and 10/18. According to the kiln operator, the process was operating under normal conditions on both of these days.

Stone size

Three different sizes of calcitic limestone were fed to the number two kiln during testing; the stone sizes were referred to as "twos", "threes", and "fours". The sizes of these stones are based on mesh size. "Twos" are stones that pass through a 1 and 3/8 inch mesh and are retained on a 7/8 inch mesh. "Threes" are stones that pass through a 7/8 inch mesh and are retained on a 3/8 inch mesh. "Fours" are stones that pass through a 3/8 inch mesh and are retained on a 3/16 inch mesh.[18] During testing, the size two stone was fed to the kiln separately while the size three and four stones were combined and fed to the kiln as one feed. The process data in Tables 2a through 2e indicate the times when the different stone sizes were fed to the kiln. The decision to use a stone size during the testing was dictated by the existing supply of the stone. Neither size two stone nor sizes three and four stones were available in a large enough supply to feed the number two kiln the same stone size during the entire three days of testing.

Table 1. Statistical Summary of Process Data Collected at Eastern Ridge Lime Company

Run 1 of Kiln 2 Scrubber Tests
10/16/96; data recorded from 3:04 pm to 8:40 pm

| Parameters for Kiln 2 | mean | std. dev. | min. | max. | # recordings |
|---|---|---|---|---|---|
| Tons of coal per hour | 3.69 | 0.1 | 3.55 | 3.78 | 21 |
| Tons of limestone per hour | 25.21 | 2.0 | 21.65 | 27.64 | 20 |
| Front end temperature (deg F) | 1741 | 48.1 | 1600 | 1826 | 21 |
| Back end temperature (deg F) | 1010.3 | 14.4 | 979.4 | 1038.1 | 21 |
| Kiln revolutions per hour | 59 | 4.8 | 50 | 64 | 21 |
| Percent oxygen at back end kiln | 1.2 | 0.8 | 0.1 | 4.1 | 21 |

Run 2 of Kiln 2 Scrubber Tests
10/17/96; data recorded from 11:42 am to 4:21 pm

| Parameters for Kiln 2 | mean | std. dev. | min. | max. | # recordings |
|---|---|---|---|---|---|
| Tons of coal per hour | 3.65 | 0.1 | 3.53 | 3.85 | 14 |
| Tons of limestone per hour | 28.16 | 0.8 | 26.66 | 29.04 | 14 |
| Front end temperature (deg F) | 1869 | 19.1 | 1840.00 | 1900 | 14 |
| Back end temperature (deg F) | 945.0 | 8.4 | 931.2 | 965.0 | 14 |
| Kiln revolutions per hour | 66 | 2.1 | 62 | 68 | 14 |
| Percent oxygen at back end kiln | 0.3 | 0.2 | 0 | 0.7 | 14 |

Run 3 of Kiln 2 Scrubber Tests
10/18/96; data recorded from 11:05 am to 3:47 pm

| Parameters for Kiln 2 | mean | std. dev. | min. | max. | # recordings |
|---|---|---|---|---|---|
| Tons of coal per hour | 3.61 | 0.0 | 3.54 | 3.71 | 15 |
| Tons of limestone per hour | 25.81 | 1.4 | 23.73 | 29.34 | 15 |
| Front end temperature (deg F) | 1840 | 15.6 | 1800.00 | 1858 | 15 |
| Back end temperature (deg F) | 1020.1 | 17.6 | 1003.6 | 1054.9 | 15 |
| Kiln revolutions per hour | 60 | 3.4 | 55 | 68 | 15 |
| Percent oxygen at back end kiln | 1.3 | 0.4 | 0.8 | 2.5 | 15 |

Run 1 of Hydrator Tests
Sat 10/19/96; data recorded from 10:00 am to 3:35 pm

| Parameters for Hydrator | mean | std. dev. | min. | max. | # recordings |
|---|---|---|---|---|---|
| Water flow rate (gal/min) | 9.6 | 0.1 | 9.4 | 9.6 | 11 |

Runs 2 & 3 of Hydrator Tests
Sun 10/20/96; data recorded from 8:00 am to 3:00 pm

| Parameters for Hydrator | mean | std. dev. | min. | max. | # recordings |
|---|---|---|---|---|---|
| Water flow rate (gal/min) | 9.5 | 0.1 | 9.4 | 9.6 | 8 |

Table 2a. Process Data

10/16/96; Run 1 of Kiln 2 Scrubber Tests
Day kiln operator = Tony
Night kiln operator = James

| | KILN PARAMETERS | | | | | |
|---|---|---|---|---|---|---|
| Time | CFR | LSFR | FET | BET | RPH | % O2 |
| 2:50 PM Kiln burners turned off for approximately 5 minutes to allow sampling probes to be inserted upstream of scrubbers; the burners were turned off to reduce the heat of the exhaust where the probes were being inserted. | | | | | | |
| currently burning small stone | | | | | | |
| 3:04 PM | 3.71 | 21.65 | 1668 | 979.4 | 50 | 1.9 |
| 3:19 PM | 3.77 | 21.74 | 1731 | 1002.7 | 50 | 1.4 |
| 3:34 PM | 3.68 | 25.68 | 1800 | 1014.5 | 60 | 1.1 |
| 3:49 PM | 3.74 | 27.08 | 1750 | 1013.3 | 64 | 1 |
| 4:04 PM | 3.7 | 27.61 | 1734 | 1007.5 | 63 | 1.1 |
| 4:19 PM | 3.74 | 27.48 | 1734 | 1007.5 | 63 | 1.1 |
| 4:34 PM | 3.78 | 27.24 | 1757 | 998 | 64 | 0.1 |
| 4:49 PM | 3.66 | 26.95 | 1719 | 1001.6 | 63 | 0.7 |
| 5:04 PM | 3.75 | 27.03 | 1319 | 989.5 | 63 | 16.5* |
| (*oxygen high because coal grate clogged up; coal feed turned off for a few minutes to unclog) | | | | | | |
| 5:12 PM | 3.73 | 27.19 | 1600 | 979.8 | 63 | 4.1 |
| Break for filter change for Method 23 | | | | | | |
| 5:40 PM | 3.72 | 24.22 | 1728 | 1004.7 | 56 | 1.1 |
| 5:55 PM | 3.72 | 24.35 | 1709 | 1012.9 | 56 | 1.5 |
| new operator came; changed to large size stone around 6:00 | | | | | | |
| 6:10 PM | 3.64 | 24.35 | 1733 | 1012.7 | 56 | 1.1 |
| 6:25 PM | 3.72 | 24.59 | 1705 | 1017.4 | 56 | 1 |
| 6:40 PM | 3.59 | 24.39 | 1732 | 1020.6 | 56 | 0.7 |
| 6:59 PM | 3.62 | | 1780 | 1028.2 | 56 | 1.5 |
| Stopped for testing change; resumed around 7:20 | | | | | | |
| 7:30 PM | 3.7 | 24.58 | 1760 | 1009.5 | 64 | 0.6 |
| 7:45 PM | 3.7 | 27.64 | 1793 | 1008.9 | 64 | 0.9 |
| 8:00 PM | 3.7 | 27.01 | 1763 | 1009.7 | 63 | 0.6 |
| 8:15 PM | 3.71 | 23.37 | 1780 | 1014.3 | 54 | 0.7 |
| 8:30 PM | 3.55 | 23.33 | 1755 | 1035.2 | 54 | 1.6 |
| 8:40 PM | 3.67 | 23.67 | 1826 | 1038.1 | 54 | 1.4 |

SCRUBBER PARAMETERS
Pressure drop of exhaust
Scrubber A Scrubber B
2.9 in. $H_2O$ 1.0 in. $H_2O$

CFR = coal feed rate (tons per hour)
LSFR = limestone feed rate (tons per hour)
FET = front end temperature of kiln (deg F)
BET = back end temperature of kiln (deg F)
RPH = kiln revolutions per hour
% O2 = percent oxygen at back end kiln

Table 2b. Process Data

10/17/96; Run 2 of Kiln 2 Scrubber Tests
Day kiln operator = Chuck

KILN PARAMETERS

| Time | CFR | LSFR | FET | BET | RPH | % O2 |
|---|---|---|---|---|---|---|
| 11:42 AM | 3.7 | 26.66 | 1860 | 965 | 62 | 0.5 |
| 12:15 PM | 3.85 | 27.57 | 1889 | 953.2 | 64 | 0.1 |
| 12:30 PM | 3.7 | 27.35 | 1860 | 952.9 | 64 | 0.3 |
| 12:51 PM | 3.7 | 27.67 | 1850 | 948.2 | 64 | 0.2 |
| 1:06 PM | 3.63 | 27.61 | 1900 | 949.1 | 64 | 0.6 |
| 1:27 PM | 3.66 | 27.58 | 1840 | 940.2 | 64 | 0.1 |
| stone size change | | | | | | |
| 1:43 PM | 3.67 | 28.19 | 1880 | 942.3 | 66 | 0.2 |
| 2:00 PM | 3.8 | 28.22 | 1880 | 931.2 | 66 | 0 |
| 2:17 PM | 3.6 | 28.95 | 1850 | 936.8 | 68 | 0.1 |
| 3:06 PM | 3.54 | 28.95 | 1850 | 939.8 | 68 | 0.4 |
| 3:21 PM | 3.53 | 28.85 | 1900 | 938.7 | 68 | 0.7 |
| 3:49 PM | 3.55 | 28.85 | 1870 | 945.6 | 68 | 0.5 |
| 4:04 PM | 3.62 | 29.04 | 1860 | 944.1 | 68 | 0.3 |
| 4:21 PM | 3.55 | 28.81 | 1870 | 942.8 | 68 | 0.3 |

SCRUBBER PARAMETERS

| Pressure drop | | Water Effluent | |
|---|---|---|---|
| Scrubber A | Scrubber B | Scrubber A | Scrubber B |
| 4.9 in. $H_2O$ | 0.9 in. $H_2O$ | 33 gal /9 se | 33 gal /15 sec |
| | | 33 gal /10 s | 33 gal /15 sec |

CFR = coal feed rate (tons per hour)
LSFR = limestone feed rate (tons per hour)
FET = front end temperature of kiln (deg F)
BET = back end temperature of kiln (deg F)
RPH = kiln revolutions per hour
% O2 = percent oxygen at back end kiln

Table 2c. Process Data

10/18/96; Run 3 of Kiln 2 Scrubber Tests
Day kiln operator = Chuck

| KILN PARAMETERS | | | | | | |
|---|---|---|---|---|---|---|
| Time | CFR | LSFR | FET | BET | RPH | % O2 |
| 11:05 AM | 3.58 | 29.34 | 1855 | 1005.1 | 68 | 1.2 |
| 11:20 AM | 1:55 PM | 27.48 | 1841 | 1003.6 | 64 | 0.9 |
| 11:40 AM | 3.6 | 26.43 | 1847 | 1008.5 | 62 | 0.8 |
| 11:57 AM | 3.69 | 25.94 | 1850 | 1006.1 | 60 | 1 |
| 12:15 PM | 3.62 | 25.77 | 1845 | 1007.2 | 60 | 1.9 |
| 12:36 PM | 3.54 | 26.12 | 1840 | 1011.8 | 60 | 2.5 |
| 12:56 PM | 2:38 PM | 25.71 | 1821 | 1015.3 | 60 | 1.2 |
| port changes; resumed around 1:35 | | | | | | |
| 1:37 PM | 3.6 | 26.22 | 1840 | 1015.8 | 60 | 1.3 |
| 1:53 PM | 3.59 | 25.68 | 1831 | 1017.2 | 60 | 0.9 |
| 2:15 PM | 3.62 | 23.99 | 1824 | 1015.4 | 55 | 1.3 |
| 2:35 PM | 3.55 | 23.94 | 1857 | 1018.3 | 55 | 1.5 |
| 2:59 PM | 3.59 | 23.73 | 1800 | 1019.6 | 55 | 1.2 |
| 3:17 PM | 3.71 | 26.06 | 1850 | 1054.9 | 60 | 1.3 |
| 3:39 PM | 3.58 | 25.43 | 1858 | 1052.7 | 60 | 1.5 |
| 3:47 PM | 3.62 | 25.34 | 1840 | 1050.5 | 60 | 1.3 |

SCRUBBER PARAMETERS
Pressure drop
Scrubber A Scrubber B
3.8 in. $H_2O$ 4.9 in. $H_2O$

CFR = coal feed rate (tons per hour)
LSFR = limestone feed rate (tons per hour)
FET = front end temperature of kiln (deg F)
BET = back end temperature of kiln (deg F)
RPH = kiln revolutions per hour
% O2 = percent oxygen at back end kiln

Table 2d. Process Data

10/19/96; Runs 1 & 2 on Hydrator*
operator = Shockey

| Time | $H_20$ flow rate to scrubber |
|---|---|
| 10:00 AM | 9.6 |
| 10:35 AM | 9.6 |
| 10:50 AM | 9.6 |
| 11:50 AM | 9.6 |
| 12:03 PM | 9.6 |
| 12:20 PM | 9.6 |
| 12:45 PM | 9.6 |
| 1:15 PM | 9.6 |
| 1:27 PM | 9.6 |
| 3:22 PM | 9.6 |
| 3:35 PM | 9.4 |

*Run 1 test data was discarded due to non isokinetic conditions

Table 2e. Process Data

10/20/96; Runs 3&4 on Hydrator
Operator = Dave

| Time | $H_20$ flow rate to scrubber |
|---|---|
| 8:00 AM | 9.6 |
| 9:00 AM | 9.6 |
| 10:00 AM | 9.6 |
| 11:00 AM | 9.6 |
| 12:00 PM | 9.4 |
| 1:00 PM | 9.4 |
| 2:00 PM | 9.4 |
| 3:00 PM | 9.4 |

Table 3. Comparison of Values of Operating Parameters Recorded During Testing to Values of Parameters Cited from Other Sources

| Operating Parameters | Average values recorded during testing | Values from standard operating and procedures manual for Eastern Ridge Lime | Values from questionnaire[1] | Values from kiln operator | Values from 1995 site survey[2] | Values from 1995 test data[3] | Values from 1989 test data[4] |
|---|---|---|---|---|---|---|---|
| Tons per hour of coal | 3.69; 3.65; 3.61 | | 2.04[5] | 3.9 - 4 | 3.96 | 4 | 4 |
| Tons per hour of limestone | 25.21; 28.16; 25.81 | | 27.85[6] | Max 27 | | | 19 |
| Tons limestone/ton lime | | | 1.91 | | | | |
| Tons coal/ton of lime | | | 0.14 | 0.33 | 0.25 - 0.33 | | |
| Kiln speed (revolutions per hour) | 59; 66; 60 | | | 55 to 65 | | 65 | |
| Back end temp. of kiln (deg F) | 1010; 945; 1020 | 1050 to 1150 (operating range)<br>1100 to 1120 (desired range) | | 1050 - 1200 | | 1100 | 928 |
| Front end temp. of kiln (deg F) | 1741; 1869; 1840 | 1200 to 1950 (operating range)<br>1700 to 1850 (desired range) | | Avg 1800 | | 1620 | 1863 |
| % $O_2$ in exhaust | 1.2; 0.3; 1.3 | 0.1 to 1 (operating range)<br>0.1 - 0.3 (desired range) | | | | | 4.5 |
| Water flow rate to hydrator scrubber (gpm) | 9.6; 9.5 | | 10 | | | | |

[1]Ref 2.

[2]Ref 1.

[3]Ref 2

[4]Ref 2

[5]Value not specified directly in questionnaire; value calculated from reported tons coal/ton of lime (0.14) and reported tons of lime per day (350).

[6]Value not specified directly in questionnaire; value calculated from reported tons of limestone/ton of lime (1.91), and reported tons of lime per day (350).

Table 4. Comparison of Calculated and Recorded Coal Feed Rates

| | Calculated coal rate (tons/hr) based on 0.14 tons coal/ton of lime[1] | Calculated coal rate (tons per hour) based on 0.33 tons coal/ton of lime[2] | Recorded average coal rate (tons per hour) during testing |
|---|---|---|---|
| Run 1 of kiln 2 scrubber tests | 1.85 | 4.36 | 3.69 |
| Run 2 of kiln 2 scrubber tests | 2.06 | 4.87 | 3.65 |
| Run 3 of kiln 2 scrubber tests | 1.89 | 4.46 | 3.61 |

[1]Equation for calculating coal feed rates based on 0.14 tons of coal / ton of lime

$$\text{calculated coal feed rate} = \frac{0.14 \text{ tons coal}}{\text{ton lime}} \text{ (questionnaire data) } \frac{\text{ton of lime}}{1.91 \text{ tons limestone}} \text{ (questionnaire data) } \frac{\text{average tons of limestone}}{\text{hr}} \text{ (recorded data)}$$

$$\text{calculated coal feed rate from run 1 of kiln 2 scrubber tests} = 0.14 * \frac{1}{1.91} * 25.21 = 1.85 \text{ tons coal per hour}$$

$$\text{calculated coal feed rate from run 2 of kiln 2 scrubber tests} = 0.14 * \frac{1}{1.91} * 28.16 = 2.06 \text{ tons coal per hour}$$

$$\text{calculated coal feed rate from run 3 of kiln 2 scrubber tests} = 0.14 * \frac{1}{1.91} * 25.81 = 1.89 \text{ tons coal per hour}$$

[2]Equation for calculating coal feed rates based on 0.33 tons of coal / ton of lime:

$$\text{calculated coal feed rate} = \frac{0.33 \text{ tons coal}}{\text{ton lime}} \text{ (kiln operator and 1995 test data) } \frac{\text{ton of lime}}{1.91 \text{ tons limestone}} \text{ (questionnaire data) } \frac{\text{average tons of limestone}}{\text{hr}} \text{ (recorded data)}$$

$$\text{calculated coal feed rate from run 1 of kiln 2 scrubber tests} = 0.33 * \frac{1}{1.91} * 25.21 = 4.36 \text{ tons coal per hour}$$

$$\text{calculated coal feed rate from run 2 of kiln 2 scrubber tests} = 0.33 * \frac{1}{1.91} * 28.16 = 4.87 \text{ tons coal per hour}$$

$$\text{calculated coal feed rate from run 3 of kiln 2 scrubber tests} = 0.33 * \frac{1}{1.91} * 25.81 = 4.46 \text{ tons coal per hour}$$

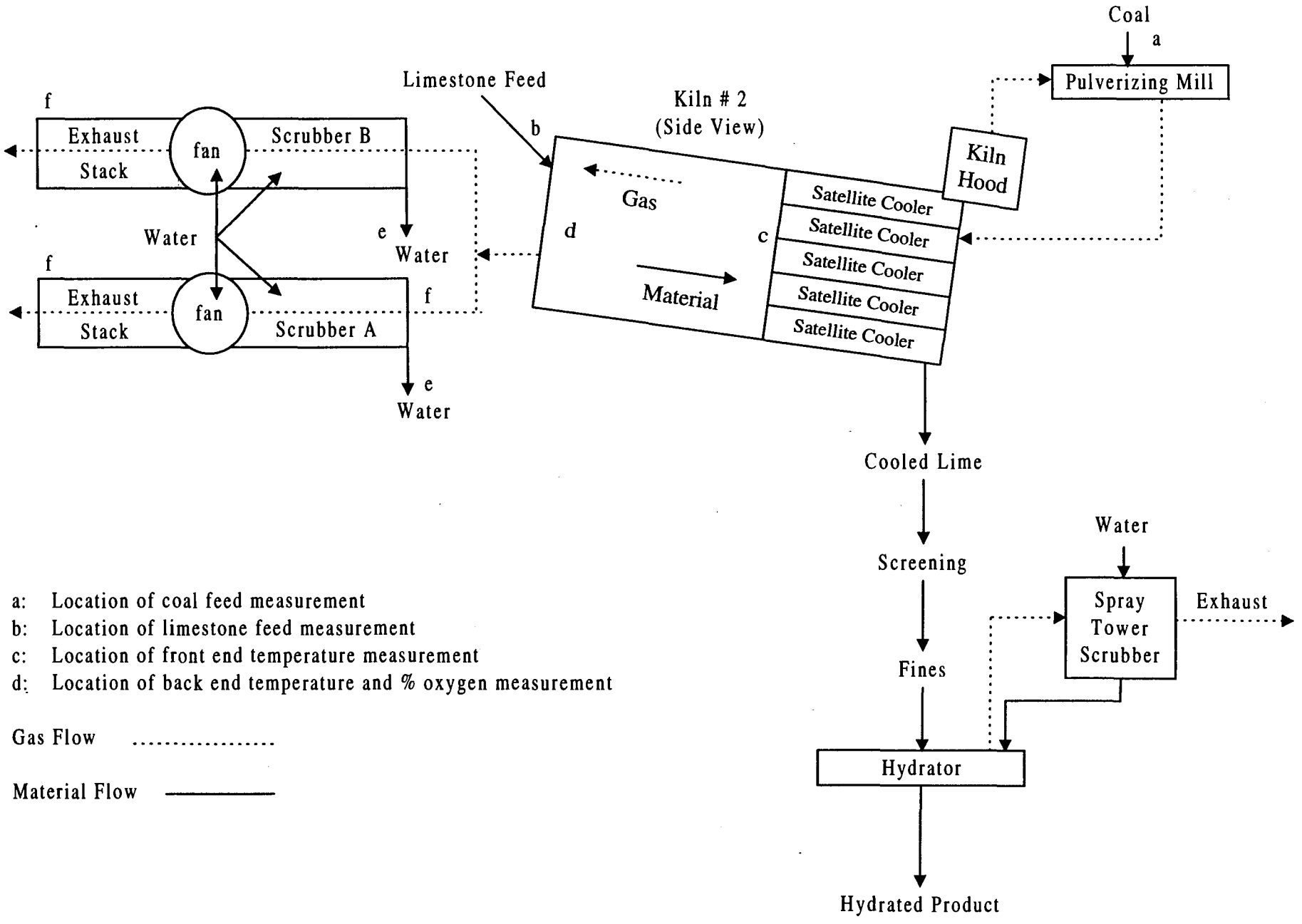
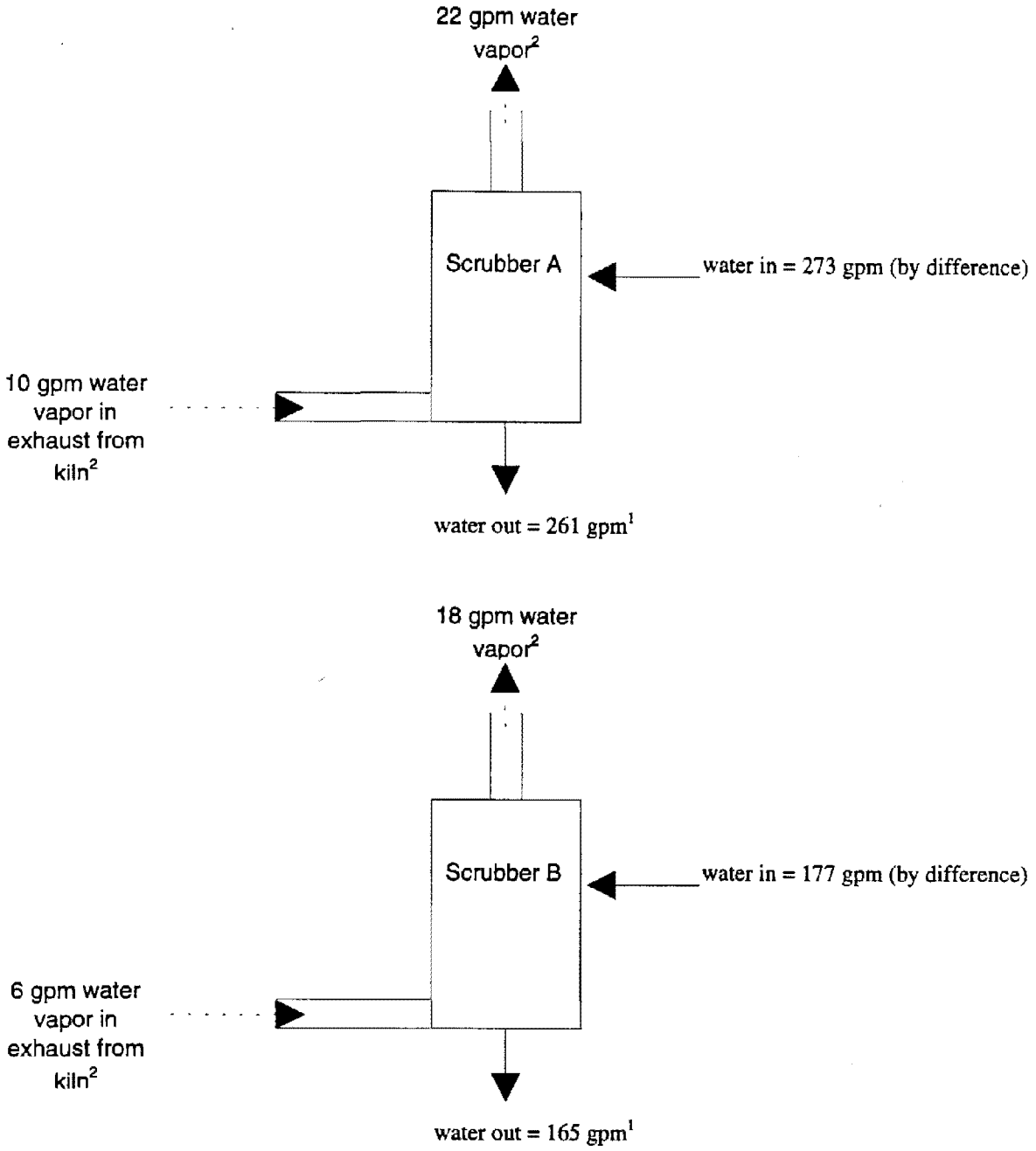



**Figure 1. Process Diagram of Kiln # 2, Hydrator, and Associated Emission Control System at Eastern Ridge Lime.**




[1]Average of two measurements taken during run 2 of kiln 2 scrubber tests
[2]Calcuated from air flow, temperature, and moisture measurements at this location during run 2 of kiln 2 scrubber tests

**Figure 2. Mass Balance of Water Across Kiln 2 Scrubbers**

REFERENCES


1. Heath, Elizabeth, Research Triangle Institute. "Site Survey of Eastern Ridge Lime, Inc., Ripplemead, Virginia." February 1, 1996.

2. Eastern Ridge response to questionnaire sent out in 1995 by the National Lime Association as part of a voluntary effort with the Environmental Protection Agency to obtain data/information for the MACT program.

3. Ref 1

4. Ref 1

5. Ref 2

6. Ref 1

7. Telecommunication between Cybele Brockmann of Research Triangle Institute and John Collins, Safety & Enviornmental director of Eastern Ridge Lime, November 21, 1996.

8. Ref 1

9. Ref 7

11. Ref 1

12. Ref 7

13. Ref 2

14. Ref 7

15. Ref 2

16. Ref 1

17. Standard Operating and Procedures Manual of Eastern Ridge Lime Plant

18. Ref 7

APPENDIX E.

EPA METHOD 320

EPA FTIR PROTOCOL

Appendix A of part 63 is amended by adding, in numerical order, Methods 320 and 321 to read as follows:

Appendix A to Part 63-Test Methods

*****

**TEST METHOD 320**

**MEASUREMENT OF VAPOR PHASE ORGANIC AND INORGANIC EMISSIONS BY EXTRACTIVE FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY**

1.0 Introduction.

Persons unfamiliar with basic elements of FTIR spectroscopy should not attempt to use this method. This method describes sampling and analytical procedures for extractive emission measurements using Fourier transform infrared (FTIR) spectroscopy. Detailed analytical procedures for interpreting infrared spectra are described in the "Protocol for the Use of Extractive Fourier Transform Infrared (FTIR) Spectrometry in Analyses of Gaseous Emissions from Stationary Sources," hereafter referred to as the "Protocol." Definitions not given in this method are given in appendix A of the Protocol. References to specific sections in the Protocol are made throughout this Method. For additional information refer to references 1 and 2, and other EPA reports, which describe the use of FTIR spectrometry in specific field measurement applications and validation tests. The sampling procedure described here is

extractive. Flue gas is extracted through a heated gas transport and handling system. For some sources, sample conditioning systems may be applicable. Some examples are given in this method. Note: sample conditioning systems may be used providing the method validation requirements in Sections 9.2 and 13.0 of this method are met.

1.1 Scope and Applicability.

1.1.1 Analytes. Analytes include hazardous air pollutants (HAPs) for which EPA reference spectra have been developed. Other compounds can also be measured with this method if reference spectra are prepared according to section 4.6 of the protocol.

1.1.2 Applicability. This method applies to the analysis of vapor phase organic or inorganic compounds which absorb energy in the mid-infrared spectral region, about 400 to 4000 $cm^{-1}$ (25 to 2.5 μm). This method is used to determine compound-specific concentrations in a multi-component vapor phase sample, which is contained in a closed-path gas cell. Spectra of samples are collected using double beam infrared absorption spectroscopy. A computer program is used to analyze spectra and report compound concentrations.

1.2 Method Range and Sensitivity. Analytical range and sensitivity depend on the frequency-dependent analyte absorptivity, instrument configuration, data collection parameters, and gas stream composition. Instrument factors

include: (a) spectral resolution, (b) interferometer signal averaging time, (c) detector sensitivity and response, and (d) absorption path length.

1.2.1 For any optical configuration the analytical range is between the absorbance values of about .01 (infrared transmittance relative to the background = 0.98) and 1.0 (T = 0.1). . (For absorbance > 1.0 the relation between absorbance and concentration may not be linear.)

1.2.2 The concentrations associated with this absorbance range depend primarily on the cell path length and the sample temperature. An analyte absorbance greater than 1.0, can be lowered by decreasing the optical path length. Analyte absorbance increases with a longer path length. Analyte detection also depends on the presence of other species exhibiting absorbance in the same analytical region. Additionally, the estimated lower absorbance (A) limit (A = 0.01) depends on the root mean square deviation (RMSD) noise in the analytical region.

1.2.3 The concentration range of this method is determined by the choice of optical configuration.

1.2.3.1 The absorbance for a given concentration can be decreased by decreasing the path length or by diluting the sample. There is no practical upper limit to the measurement range.

1.2.3.2 The analyte absorbance for a given concentration

may be increased by increasing the cell path length or (to some extent) using a higher resolution. Both modifications also cause a corresponding increased absorbance for all compounds in the sample, and a decrease in the signal throughput. For this reason the practical lower detection range (quantitation limit) usually depends on sample characteristics such as moisture content of the gas, the presence of other interferants, and losses in the sampling system.

1.3 Sensitivity. The limit of sensitivity for an optical configuration and integration time is determined using appendix D of the Protocol: Minimum Analyte Uncertainty, (MAU). The MAU depends on the RMSD noise in an analytical region, and on the absorptivity of the analyte in the same region.

1.4 Data Quality. Data quality shall be determined by executing Protocol pre-test procedures in appendices B to H of the protocol and post-test procedures in appendices I and J of the protocol.

1.4.1 Measurement objectives shall be established by the choice of detection limit ($DL_i$) and analytical uncertainty ($AU_i$) for each analyte.

1.4.2 An instrumental configuration shall be selected. An estimate of gas composition shall be made based on previous test data, data from a similar source or information

gathered in a pre-test site survey. Spectral interferants shall be identified using the selected $DL_i$ and $AU_i$ and band areas from reference spectra and interferant spectra. The baseline noise of the system shall be measured in each analytical region to determine the MAU of the instrument configuration for each analyte and interferant ($MIU_i$).

1.4.3 Data quality for the application shall be determined, in part, by measuring the RMS (root mean square) noise level in each analytical spectral region (appendix C of the Protocol). The RMS noise is defined as the RMSD of the absorbance values in an analytical region from the mean absorbance value in the region.

1.4.4 The MAU is the minimum analyte concentration for which the $AU_i$ can be maintained; if the measured analyte concentration is less than $MAU_i$, then data quality are unacceptable.

2.0 Summary of Method.

2.1 Principle. References 4 through 7 provide background material on infrared spectroscopy and quantitative analysis. A summary is given in this section.

2.1.1 Infrared absorption spectroscopy is performed by directing an infrared beam through a sample to a detector. The frequency-dependent infrared absorbance of the sample is measured by comparing this detector signal (single beam spectrum) to a signal obtained without a sample in the beam

path (background).

2.1.2 Most molecules absorb infrared radiation and the absorbance occurs in a characteristic and reproducible pattern. The infrared spectrum measures fundamental molecular properties and a compound can be identified from its infrared spectrum alone.

2.1.3 Within constraints, there is a linear relationship between infrared absorption and compound concentration. If this frequency dependent relationship (absorptivity) is known (measured), it can be used to determine compound concentration in a sample mixture.

2.1.4 Absorptivity is measured by preparing, in the laboratory, standard samples of compounds at known concentrations and measuring the FTIR "reference spectra" of these standard samples. These "reference spectra" are then used in sample analysis: (1) compounds are detected by matching sample absorbance bands with bands in reference spectra, and (2) concentrations are measured by comparing sample band intensities with reference band intensities.

2.1.5 This method is self-validating provided that the results meet the performance requirement of the QA spike in sections 8.6.2 and 9.0 of this method, and results from a previous method validation study support the use of this method in the application.

2.2 Sampling and Analysis. In extractive sampling a probe

assembly and pump are used to extract gas from the exhaust of the affected source and transport the sample to the FTIR gas cell. Typically, the sampling apparatus is similar to that used for single-component continuous emission monitor (CEM) measurements.

2.2.1 The digitized infrared spectrum of the sample in the FTIR gas cell is measured and stored on a computer. Absorbance band intensities in the spectrum are related to sample concentrations by what is commonly referred to as Beer's Law.

$$A_i = a_i b c_i \qquad \textbf{(1)}$$

where:

$A_i$ = absorbance at a given frequency of the ith sample component.

$a_i$ = absorption coefficient (absorptivity) of the ith sample component.

$b$ = path length of the cell.

$c_i$ = concentration of the ith sample component.

2.2.2 Analyte spiking is used for quality assurance (QA). In this procedure (section 8.6.2 of this method) an analyte is spiked into the gas stream at the back end of the sample probe. Analyte concentrations in the spiked samples are compared to analyte concentrations in unspiked samples.

Since the concentration of the spike is known, this procedure can be used to determine if the sampling system is removing the spiked analyte(s) from the sample stream.

2.3 Reference Spectra Availability. Reference spectra of over 100 HAPs are available in the EPA FTIR spectral library on the EMTIC (Emission Measurement Technical Information Center) computer bulletin board service and at internet address http://info.arnold.af.mil/epa/welcome.htm. Reference spectra for HAPs, or other analytes, may also be prepared according to section 4.6 of the Protocol.

2.4 Operator Requirements. The FTIR analyst shall be trained in setting up the instrumentation, verifying the instrument is functioning properly, and performing routine maintenance. The analyst must evaluate the initial sample spectra to determine if the sample matrix is consistent with pre-test assumptions and if the instrument configuration is suitable. The analyst must be able to modify the instrument configuration, if necessary.

2.4.1 The spectral analysis shall be supervised by someone familiar with EPA FTIR Protocol procedures.

2.4.2 A technician trained in instrumental test methods is qualified to install and operate the sampling system. This includes installing the probe and heated line assembly, operating the analyte spike system, and performing moisture and flow measurements.

3.0 Definitions.

See appendix A of the Protocol for definitions relating to infrared spectroscopy. Additional definitions are given in sections 3.1 through 3.29.

3.1 Analyte. A compound that this method is used to measure. The term "target analyte" is also used. This method is multi-component and a number of analytes can be targeted for a test.

3.2 Reference Spectrum. Infrared spectrum of an analyte prepared under controlled, documented, and reproducible laboratory conditions according to procedures in section 4.6 of the Protocol. A library of reference spectra is used to measure analytes in gas samples.

3.3 Standard Spectrum. A spectrum that has been prepared from a reference spectrum through a (documented) mathematical operation. A common example is de-resolving of reference spectra to lower-resolution standard spectra (Protocol, appendix K to the addendum of this method). Standard spectra, prepared by approved, and documented, procedures can be used as reference spectra for analysis.

3.4 Concentration. In this method concentration is expressed as a molar concentration, in ppm-meters, or in (ppm-meters)/K, where K is the absolute temperature (Kelvin). The latter units allow the direct comparison of concentrations from systems using different optical

configurations or sampling temperatures.

3.5 Interferant. A compound in the sample matrix whose infrared spectrum overlaps with part of an analyte spectrum. The most accurate analyte measurements are achieved when reference spectra of interferants are used in the quantitative analysis with the analyte reference spectra. The presence of an interferant can increase the analytical uncertainty in the measured analyte concentration.

3.6 Gas Cell. A gas containment cell that can be evacuated. It is equipped with the optical components to pass the infrared beam through the sample to the detector. Important cell features include: path length (or range if variable), temperature range, materials of construction, and total gas volume.

3.7 Sampling System. Equipment used to extract the sample from the test location and transport the sample gas to the FTIR analyzer. This includes sample conditioning systems.

3.8 Sample Analysis. The process of interpreting the infrared spectra to obtain sample analyte concentrations. This process is usually automated using a software routine employing a classical least squares (cls), partial least squares (pls), or K- or P- matrix method.

3.9 One hundred percent line. A double beam transmittance spectrum obtained by combining two background single beam spectra. Ideally, this line is equal to 100 percent

transmittance (or zero absorbance) at every frequency in the spectrum. Practically, a zero absorbance line is used to measure the baseline noise in the spectrum.

3.10 Background Deviation. A deviation from 100 percent transmittance in any region of the 100 percent line. Deviations greater than ± 5 percent in an analytical region are unacceptable (absorbance of 0.021 to -0.022). Such deviations indicate a change in the instrument throughput relative to the background single beam.

3.11 Batch Sampling. A procedure where spectra of discreet, static samples are collected. The gas cell is filled with sample and the cell is isolated. The spectrum is collected. Finally, the cell is evacuated to prepare for the next sample.

3.12 Continuous Sampling. A procedure where spectra are collected while sample gas is flowing through the cell at a measured rate.

3.13 Sampling resolution. The spectral resolution used to collect sample spectra.

3.14 Truncation. Limiting the number of interferogram data points by deleting points farthest from the center burst (zero path difference, ZPD).

3.15 Zero filling. The addition of points to the interferogram. The position of each added point is interpolated from neighboring real data points. Zero

filling adds no information to the interferogram, but affects line shapes in the absorbance spectrum (and possibly analytical results).

3.16 Reference CTS. Calibration Transfer Standard spectra that were collected with reference spectra.

3.17 CTS Standard. CTS spectrum produced by applying a de-resolution procedure to a reference CTS.

3.18 Test CTS. CTS spectra collected at the sampling resolution using the same optical configuration as for sample spectra. Test spectra help verify the resolution, temperature and path length of the FTIR system.

3.19 RMSD. Root Mean Square Difference, defined in EPA FTIR Protocol, appendix A.

3.20 Sensitivity. The noise-limited compound-dependent detection limit for the FTIR system configuration. This is estimated by the MAU. It depends on the RMSD in an analytical region of a zero absorbance line.

3.21 Quantitation Limit. The lower limit of detection for the FTIR system configuration in the sample spectra. This is estimated by mathematically subtracting scaled reference spectra of analytes and interferences from sample spectra, then measuring the RMSD in an analytical region of the subtracted spectrum. Since the noise in subtracted sample spectra may be much greater than in a zero absorbance spectrum, the quantitation limit is generally much higher

than the sensitivity. Removing spectral interferences from the sample or improving the spectral subtraction can lower the quantitation limit toward (but not below) the sensitivity.

3.22 Independent Sample. A unique volume of sample gas; there is no mixing of gas between two consecutive independent samples. In continuous sampling two independent samples are separated by at least 5 cell volumes. The interval between independent measurements depends on the cell volume and the sample flow rate (through the cell).

3.23 Measurement. A single spectrum of flue gas contained in the FTIR cell.

3.24 Run. A run consists of a series of measurements. At a minimum a run includes 8 independent measurements spaced over 1 hour.

3.25 Validation. Validation of FTIR measurements is described in sections 13.0 through 13.4 of this method. Validation is used to verify the test procedures for measuring specific analytes at a source. Validation provides proof that the method works under certain test conditions.

3.26 Validation Run. A validation run consists of at least 24 measurements of independent samples. Half of the samples are spiked and half are not spiked. The length of the run is determined by the interval between independent samples.

3.27 Screening. Screening is used when there is little or no available information about a source. The purpose of screening is to determine what analytes are emitted and to obtain information about important sample characteristics such as moisture, temperature, and interferences. Screening results are semi-quantitative (estimated concentrations) or qualitative (identification only). Various optical and sampling configurations may be used. Sample conditioning systems may be evaluated for their effectiveness in removing interferences. It is unnecessary to perform a complete run under any set of sampling conditions. Spiking is not necessary, but spiking can be a useful screening tool for evaluating the sampling system, especially if a reactive or soluble analyte is used for the spike.

3.28 Emissions Test. An FTIR emissions test is performed according specific sampling and analytical procedures. These procedures, for the target analytes and the source, are based on previous screening and validation results. Emission results are quantitative. A QA spike (sections 8.6.2 and 9.2 of this method) is performed under each set of sampling conditions using a representative analyte. Flow, gas temperature and diluent data are recorded concurrently with the FTIR measurements to provide mass emission rates for detected compounds.

3.29 Surrogate. A surrogate is a compound that is used in

a QA spike procedure (section 8.6.2 of this method) to represent other compounds. The chemical and physical properties of a surrogate shall be similar to the compounds it is chosen to represent. Under given sampling conditions, usually a single sampling factor is of primary concern for measuring the target analytes: for example, the surrogate spike results can be representative for analytes that are more reactive, more soluble, have a lower absorptivity, or have a lower vapor pressure than the surrogate itself.

4.0 Interferences.

Interferences are divided into two classifications: analytical and sampling.

4.1 Analytical Interferences. An analytical interference is a spectral feature that complicates (in extreme cases may prevent) the analysis of an analyte. Analytical interferences are classified as background or spectral interference.

4.1.1 Background Interference. This results from a change in throughput relative to the single beam background. It is corrected by collecting a new background and proceeding with the test. In severe instances the cause must be identified and corrected. Potential causes include: (1) deposits on reflective surfaces or transmitting windows, (2) changes in detector sensitivity, (3) a change in the infrared source output, or (4) failure in the instrument electronics. In

routine sampling throughput may degrade over several hours. Periodically a new background must be collected, but no other corrective action will be required.

4.1.2 Spectral Interference. This results from the presence of interfering compound(s) (interferant) in the sample. Interferant spectral features overlap analyte spectral features. Any compound with an infrared spectrum, including analytes, can potentially be an interferant. The Protocol measures absorbance band overlap in each analytical region to determine if potential interferants shall be classified as known interferants (FTIR Protocol, section 4.9 and appendix B). Water vapor and $CO_2$ are common spectral interferants. Both of these compounds have strong infrared spectra and are present in many sample matrices at high concentrations relative to analytes. The extent of interference depends on the (1) interferant concentration, (2) analyte concentration, and (3) the degree of band overlap. Choosing an alternate analytical region can minimize or avoid the spectral interference. For example, $CO_2$ interferes with the analysis of the 670 $cm^{-1}$ benzene band. However, benzene can also be measured near 3000 $cm^{-1}$ (with less sensitivity).

4.2 Sampling System Interferences. These prevent analytes from reaching the instrument. The analyte spike procedure is designed to measure sampling system interference, if any.

4.2.1 Temperature. A temperature that is too low causes condensation of analytes or water vapor. The materials of the sampling system and the FTIR gas cell usually set the upper limit of temperature.

4.2.2 Reactive Species. Anything that reacts with analytes. Some analytes, like formaldehyde, polymerize at lower temperatures.

4.2.3 Materials. Poor choice of material for probe, or sampling line may remove some analytes. For example, HF reacts with glass components.

4.2.4 Moisture. In addition to being a spectral interferant, condensed moisture removes soluble compounds.

5.0 Safety.

The hazards of performing this method are those associated with any stack sampling method and the same precautions shall be followed. Many HAPs are suspected carcinogens or present other serious health risks. Exposure to these compounds should be avoided in all circumstances. For instructions on the safe handling of any particular compound, refer to its material safety data sheet. When using analyte standards, always ensure that gases are properly vented and that the gas handling system is leak free. (Always perform a leak check with the system under maximum vacuum and, again, with the system at greater than ambient pressure.) Refer to section 8.2 of this method for

leak check procedures. This method does not address all of the potential safety risks associated with its use. Anyone performing this method must follow safety and health practices consistent with applicable legal requirements and with prudent practice for each application.

6.0 Equipment and Supplies.

Note: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

The equipment and supplies are based on the schematic of a sampling system shown in Figure 1. Either the batch or continuous sampling procedures may be used with this sampling system. Alternative sampling configurations may also be used, provided that the data quality objectives are met as determined in the post-analysis evaluation. Other equipment or supplies may be necessary, depending on the design of the sampling system or the specific target analytes.

6.1 Sampling Probe. Glass, stainless steel, or other appropriate material of sufficient length and physical integrity to sustain heating, prevent adsorption of analytes, and to transport analytes to the infrared gas cell. Special materials or configurations may be required in some applications. For instance, high stack sample temperatures may require special steel or cooling the probe.

For very high moisture sources it may be desirable to use a dilution probe.

6.2 Particulate Filters. A glass wool plug (optional) inserted at the probe tip (for large particulate removal) and a filter (required) rated for 99 percent removal efficiency at 1-micron (e.g., Balston™) connected at the outlet of the heated probe.

6.3 Sampling Line/Heating System. Heated (sufficient to prevent condensation) stainless steel, polytetrafluoroethane, or other material inert to the analytes.

6.4 Gas Distribution Manifold. A heated manifold allowing the operator to control flows of gas standards and samples directly to the FTIR system or through sample conditioning systems. Usually includes heated flow meter, heated valve for selecting and sending sample to the analyzer, and a by-pass vent. This is typically constructed of stainless steel tubing and fittings, and high-temperature valves.

6.5 Stainless Steel Tubing. Type 316, appropriate diameter (e.g., 3/8 in.) and length for heated connections. Higher grade stainless may be desirable in some applications.

6.6 Calibration/Analyte Spike Assembly. A three way valve assembly (or equivalent) to introduce analyte or surrogate spikes into the sampling system at the outlet of the probe upstream of the out-of-stack particulate filter and the FTIR

analytical system.

6.7 Mass Flow Meter (MFM). These are used for measuring analyte spike flow. The MFM shall be calibrated in the range of 0 to 5 L/min and be accurate to ± 2 percent (or better) of the flow meter span.

6.8 Gas Regulators. Appropriate for individual gas standards.

6.9 Polytetrafluoroethane Tubing. Diameter (e.g., 3/8 in.) and length suitable to connect cylinder regulators to gas standard manifold.

6.10 Sample Pump. A leak-free pump (e.g., KNF™), with by-pass valve, capable of producing a sample flow rate of at least 10 L/min through 100 ft of sample line. If the pump is positioned upstream of the distribution manifold and FTIR system, use a heated pump that is constructed from materials non-reactive to the analytes. If the pump is located downstream of the FTIR system, the gas cell sample pressure will be lower than ambient pressure and it must be recorded at regular intervals.

6.11 Gas Sample Manifold. Secondary manifold to control sample flow at the inlet to the FTIR manifold. This is optional, but includes a by-pass vent and heated rotameter.

6.12 Rotameter. A 0 to 20 L/min rotameter. This meter need not be calibrated.

6.13 FTIR Analytical System. Spectrometer and detector,

capable of measuring the analytes to the chosen detection limit. The system shall include a personal computer with compatible software allowing automated collection of spectra.

6.14 FTIR Cell Pump. Required for the batch sampling technique, capable of evacuating the FTIR cell volume within 2 minutes. The pumping speed shall allow the operator to obtain 8 sample spectra in 1 hour.

6.15 Absolute Pressure Gauge. Capable of measuring pressure from 0 to 1000 mmHg to within ± 2.5 mmHg (e.g., Baratron™).

6.16 Temperature Gauge. Capable of measuring the cell temperature to within ± 2°C.

6.17 Sample Conditioning. One option is a condenser system, which is used for moisture removal. This can be helpful in the measurement of some analytes. Other sample conditioning procedures may be devised for the removal of moisture or other interfering species.

6.17.1 The analyte spike procedure of section 9.2 of this method, the QA spike procedure of section 8.6.2 of this method, and the validation procedure of section 13 of this method demonstrate whether the sample conditioning affects analyte concentrations. Alternatively, measurements can be made with two parallel FTIR systems; one measuring conditioned sample, the other measuring unconditioned

sample.

6.17.2 Another option is sample dilution. The dilution factor measurement must be documented and accounted for in the reported concentrations. An alternative to dilution is to lower the sensitivity of the FTIR system by decreasing the cell path length, or to use a short-path cell in conjunction with a long path cell to measure more than one concentration range.

7.0 Reagents and Standards.

7.1 Analyte(s) and Tracer Gas. Obtain a certified gas cylinder mixture containing all of the analyte(s) at concentrations within ± 2 percent of the emission source levels (expressed in ppm-meter/K). If practical, the analyte standard cylinder shall also contain the tracer gas at a concentration which gives a measurable absorbance at a dilution factor of at least 10:1. Two ppm $SF_6$ is sufficient for a path length of 22 meters at 250 °F.

7.2 Calibration Transfer Standard(s). Select the calibration transfer standards (CTS) according to section 4.5 of the FTIR Protocol. Obtain a National Institute of Standards and Technology (NIST) traceable gravimetric standard of the CTS (± 2 percent).

7.3 Reference Spectra. Obtain reference spectra for each analyte, interferant, surrogate, CTS, and tracer. If EPA reference spectra are not available, use reference spectra

prepared according to procedures in section 4.6 of the EPA FTIR Protocol.

8.0 Sampling and Analysis Procedure.

Three types of testing can be performed: (1) screening, (2) emissions test, and (3) validation. Each is defined in section 3 of this method. Determine the purpose(s) of the FTIR test. Test requirements include: (a) $AU_i$, $DL_i$, overall fractional uncertainty, $OFU_i$, maximum expected concentration ($CMAX_i$), and $t_{AN}$ for each, (b) potential interferants, (c) sampling system factors, e.g., minimum absolute cell pressure, ($P_{min}$), FTIR cell volume ($V_{ss}$), estimated sample absorption pathlength, $L_s'$, estimated sample pressure, $P_s'$, $T_s'$, signal integration time ($t_{ss}$), minimum instrumental linewidth, MIL, fractional error, and (d) analytical regions, e.g., m = 1 to M, lower wavenumber position, $FL_m$, center wavenumber position, $FC_m$, and upper wavenumber position, $FU_m$, plus interferants, upper wavenumber position of the CTS absorption band, $FFU_m$, lower wavenumber position of the CTS absorption band, $FFL_m$, wavenumber range FNU to FNL. If necessary, sample and acquire an initial spectrum. From analysis of this preliminary spectrum determine a suitable operational path length. Set up the sampling train as shown in Figure 1 or use an appropriate alternative configuration. Sections 8.1 through 8.11 of this method provide guidance on pre-test calculations in the EPA

protocol, sampling and analytical procedures, and post-test protocol calculations.

8.1 Pretest Preparations and Evaluations. Using the procedure in section 4.0 of the FTIR Protocol, determine the optimum sampling system configuration for measuring the target analytes. Use available information to make reasonable assumptions about moisture content and other interferences.

8.1.1 Analytes. Select the required detection limit ($DL_i$) and the maximum permissible analytical uncertainty ($AU_i$) for each analyte (labeled from 1 to i). Estimate, if possible, the maximum expected concentration for each analyte, $CMAX_i$. The expected measurement range is fixed by $DL_i$ and $CMAX_i$ for each analyte (i).

8.1.2 Potential Interferants. List the potential interferants. This usually includes water vapor and $CO_2$, but may also include some analytes and other compounds.

8.1.3. Optical Configuration. Choose an optical configuration that can measure all of the analytes within the absorbance range of .01 to 1.0 (this may require more than one path length). Use Protocol sections 4.3 to 4.8 for guidance in choosing a configuration and measuring CTS.

8.1.4. Fractional Reproducibility Uncertainty ($FRU_i$). The FRU is determined for each analyte by comparing CTS spectra taken before and after the reference spectra were measured.

The EPA para-xylene reference spectra were collected on 10/31/91 and 11/01/91 with corresponding CTS spectra "cts1031a," and "cts1101b." The CTS spectra are used to estimate the reproducibility (FRU) in the system that was used to collect the references. The FRU must be < AU. Appendix E of the protocol is used to calculate the FRU from CTS spectra. Figure 2 plots results for 0.25 $cm^{-1}$ CTS spectra in EPA reference library: $S_3$ (cts1101b - cts1031a), and $S_4$ [(cts1101b + cts1031a)/2]. The RMSD (SRMS) is calculated in the subtracted baseline, $S_3$, in the corresponding CTS region from 850 to 1065 $cm^{-1}$. The area (BAV) is calculated in the same region of the averaged CTS spectrum, $S_4$.

8.1.5 Known Interferants. Use appendix B of the EPA FTIR Protocol.

8.1.6 Calculate the Minimum Analyte Uncertainty, MAU (section 1.3 of this method discusses MAU and protocol appendix D gives the MAU procedure). The MAU for each analyte, i, and each analytical region, m, depends on the RMS noise.

8.1.7 Analytical Program. See FTIR Protocol, section 4.10. Prepare computer program based on the chosen analytical technique. Use as input reference spectra of all target analytes and expected interferants. Reference spectra of additional compounds shall also be included in the program

if their presence (even if transient) in the samples is considered possible. The program output shall be in ppm (or ppb) and shall be corrected for differences between the reference path length, $L_R$, temperature, $T_R$, and pressure, $P_R$, and the conditions used for collecting the sample spectra. If sampling is performed at ambient pressure, then any pressure correction is usually small relative to corrections for path length and temperature, and may be neglected.

8.2 Leak-check.

8.2.1 Sampling System. A typical FTIR extractive sampling train is shown in Figure 1. Leak check from the probe tip to pump outlet as follows: Connect a 0- to 250-mL/min rate meter (rotameter or bubble meter) to the outlet of the pump. Close off the inlet to the probe, and record the leak rate. The leak rate shall be ≤ 200 mL/min.

8.2.2 Analytical System Leak check. Leak check the FTIR cell under vacuum and under pressure (greater than ambient). Leak check connecting tubing and inlet manifold under pressure.

8.2.2.1 For the evacuated sample technique, close the valve to the FTIR cell, and evacuate the absorption cell to the minimum absolute pressure $P_{min}$. Close the valve to the pump, and determine the change in pressure $\Delta P_v$ after 2 minutes.

8.2.2.2 For both the evacuated sample and purging techniques, pressurize the system to about 100 mmHg above

atmospheric pressure. Isolate the pump and determine the change in pressure $\Delta P_p$ after 2 minutes.

8.2.2.3 Measure the barometric pressure, $P_b$ in mmHg.

8.2.2.4 Determine the percent leak volume $\%V_L$ for the signal integration time $t_{ss}$ and for $\Delta P_{max}$, i.e., the larger of $\Delta P_v$ or $\Delta P_p$, as follows:

$$\%V_L = 50\, t_{SS}\, \frac{\Delta P_{max}}{P_{SS}} \qquad (2)$$

where 50 = 100% divided by the leak-check time of 2 minutes.

8.2.2.5 Leak volumes in excess of 4 percent of the FTIR system volume $V_{ss}$ are unacceptable.

8.3 Detector Linearity. Once an optical configuration is chosen, use one of the procedures of sections 8.3.1 through 8.3.3 to verify that the detector response is linear. If the detector response is not linear, decrease the aperture, or attenuate the infrared beam. After a change in the instrument configuration perform a linearity check until it is demonstrated that the detector response is linear.

8.3.1 Vary the power incident on the detector by modifying the aperture setting. Measure the background and CTS at three instrument aperture settings: (1) at the aperture setting to be used in the testing, (2) at one half this aperture and (3) at twice the proposed testing aperture.

Compare the three CTS spectra. CTS band areas shall agree to within the uncertainty of the cylinder standard and the RMSD noise in the system. If test aperture is the maximum aperture, collect CTS spectrum at maximum aperture, then close the aperture to reduce the IR throughput by half. Collect a second background and CTS at the smaller aperture setting and compare the spectra again.

8.3.2 Use neutral density filters to attenuate the infrared beam. Set up the FTIR system as it will be used in the test measurements. Collect a CTS spectrum. Use a neutral density filter to attenuate the infrared beam (either immediately after the source or the interferometer) to approximately 1/2 its original intensity. Collect a second CTS spectrum. Use another filter to attenuate the infrared beam to approximately 1/4 its original intensity. Collect a third background and CTS spectrum. Compare the CTS spectra. CTS band areas shall agree to within the uncertainty of the cylinder standard and the RMSD noise in the system.

8.3.3 Observe the single beam instrument response in a frequency region where the detector response is known to be zero. Verify that the detector response is "flat" and equal to zero in these regions.

8.4 Data Storage Requirements. All field test spectra shall be stored on a computer disk and a second backup copy must stored on a separate disk. The stored information

includes sample interferograms, processed absorbance spectra, background interferograms, CTS sample interferograms and CTS absorbance spectra. Additionally, documentation of all sample conditions, instrument settings, and test records must be recorded on hard copy or on computer medium. Table 1 gives a sample presentation of documentation.

8.5 Background Spectrum. Evacuate the gas cell to ≤ 5 mmHg, and fill with dry nitrogen gas to ambient pressure (or purge the cell with 10 volumes of dry nitrogen). Verify that no significant amounts of absorbing species (for example water vapor and $CO_2$) are present. Collect a background spectrum, using a signal averaging period equal to or greater than the averaging period for the sample spectra. Assign a unique file name to the background spectrum. Store two copies of the background interferogram and processed single-beam spectrum on separate computer disks (one copy is the back-up).

8.5.1 Interference Spectra. If possible, collect spectra of known and suspected major interferences using the same optical system that will be used in the field measurements. This can be done on-site or earlier. A number of gases, e.g. $CO_2$, $SO_2$, CO, $NH_3$, are readily available from cylinder gas suppliers.

8.5.2 Water vapor spectra can be prepared by the following

procedure. Fill a sample tube with distilled water. Evacuate above the sample and remove dissolved gasses by alternately freezing and thawing the water while evacuating. Allow water vapor into the FTIR cell, then dilute to atmospheric pressure with nitrogen or dry air. If quantitative water spectra are required, follow the reference spectrum procedure for neat samples (protocol, section 4.6). Often, interference spectra need not be quantitative, but for best results the absorbance must be comparable to the interference absorbance in the sample spectra.

8.6 Pre-Test Calibrations

8.6.1 Calibration Transfer Standard. Evacuate the gas cell to ≤ 5 mmHg absolute pressure, and fill the FTIR cell to atmospheric pressure with the CTS gas. Alternatively, purge the cell with 10 cell volumes of CTS gas. (If purge is used, verify that the CTS concentration in the cell is stable by collecting two spectra 2 minutes apart as the CTS gas continues to flow. If the absorbance in the second spectrum is no greater than in the first, within the uncertainty of the gas standard, then this can be used as the CTS spectrum.) Record the spectrum.

8.6.2 QA Spike. This procedure assumes that the method has been validated for at least some of the target analytes at the source. For emissions testing perform a QA spike. Use

a certified standard, if possible, of an analyte, which has been validated at the source. One analyte standard can serve as a QA surrogate for other analytes which are less reactive or less soluble than the standard. Perform the spike procedure of section 9.2 of this method. Record spectra of at least three independent (section 3.22 of this method) spiked samples. Calculate the spiked component of the analyte concentration. If the average spiked concentration is within 0.7 to 1.3 times the expected concentration, then proceed with the testing. If applicable, apply the correction factor from the Method 301 of this appendix validation test (not the result from the QA spike).

8.7 Sampling. If analyte concentrations vary rapidly with time, continuous sampling is preferable using the smallest cell volume, fastest sampling rate and fastest spectra collection rate possible. Continuous sampling requires the least operator intervention even without an automated sampling system. For continuous monitoring at one location over long periods, Continuous sampling is preferred. Batch sampling and continuous static sampling are used for screening and performing test runs of finite duration. Either technique is preferred for sampling several locations in a matter of days. Batch sampling gives reasonably good time resolution and ensures that each spectrum measures a

discreet (and unique) sample volume. Continuous static (and continuous) sampling provide a very stable background over long periods. Like batch sampling, continuous static sampling also ensures that each spectrum measures a unique sample volume. It is essential that the leak check procedure under vacuum (section 8.2 of this method) is passed if the batch sampling procedure is used. It is essential that the leak check procedure under positive pressure is passed if the continuous static or continuous sampling procedures are used. The sampling techniques are described in sections 8.7.1 through 8.7.2 of this method.

8.7.1 Batch Sampling. Evacuate the absorbance cell to ≤ 5 mmHg absolute pressure. Fill the cell with exhaust gas to ambient pressure, isolate the cell, and record the spectrum. Before taking the next sample, evacuate the cell until no spectral evidence of sample absorption remains. Repeat this procedure to collect eight spectra of separate samples in 1 hour.

8.7.2 Continuous Static Sampling. Purge the FTIR cell with 10 cell volumes of sample gas. Isolate the cell, collect the spectrum of the static sample and record the pressure. Before measuring the next sample, purge the cell with 10 more cell volumes of sample gas.

8.8 Sampling QA and Reporting.

8.8.1 Sample integration times shall be sufficient to

achieve the required signal-to-noise ratio. Obtain an absorbance spectrum by filling the cell with $N_2$. Measure the RMSD in each analytical region in this absorbance spectrum. Verify that the number of scans used is sufficient to achieve the target MAU.

8.8.2 Assign a unique file name to each spectrum.

8.8.3 Store two copies of sample interferograms and processed spectra on separate computer disks.

8.8.4 For each sample spectrum, document the sampling conditions, the sampling time (while the cell was being filled), the time the spectrum was recorded, the instrumental conditions (path length, temperature, pressure, resolution, signal integration time), and the spectral file name. Keep a hard copy of these data sheets.

8.9 Signal Transmittance. While sampling, monitor the signal transmittance. If signal transmittance (relative to the background) changes by 5 percent or more (absorbance = -.02 to .02) in any analytical spectral region, obtain a new background spectrum.

8.10 Post-test CTS. After the sampling run, record another CTS spectrum.

8.11 Post-test QA.

8.11.1 Inspect the sample spectra immediately after the run to verify that the gas matrix composition was close to the expected (assumed) gas matrix.

8.11.2 Verify that the sampling and instrumental parameters were appropriate for the conditions encountered. For example, if the moisture is much greater than anticipated, it may be necessary to use a shorter path length or dilute the sample.

8.11.3 Compare the pre- and post-test CTS spectra. The peak absorbance in pre- and post-test CTS must be ± 5 percent of the mean value. See appendix E of the FTIR Protocol.

9.0 Quality Control.

Use analyte spiking (sections 8.6.2, 9.2 and 13.0 of this method) to verify that the sampling system can transport the analytes from the probe to the FTIR system.

9.1 Spike Materials. Use a certified standard (accurate to ± 2 percent) of the target analyte, if one can be obtained. If a certified standard cannot be obtained, follow the procedures in section 4.6.2.2 of the FTIR Protocol.

9.2 Spiking Procedure. QA spiking (section 8.6.2 of this method) is a calibration procedure used before testing. QA spiking involves following the spike procedure of sections 9.2.1 through 9.2.3 of this method to obtain at least three spiked samples. The analyte concentrations in the spiked samples shall be compared to the expected spike concentration to verify that the sampling/analytical system is working properly. Usually, when QA spiking is used, the

method has already been validated at a similar source for the analyte in question. The QA spike demonstrates that the validated sampling/analytical conditions are being duplicated. If the QA spike fails then the sampling/analytical system shall be repaired before testing proceeds. The method validation procedure (section 13.0 of this method) involves a more extensive use of the analyte spike procedure of sections 9.2.1 through 9.2.3 of this method. Spectra of at least 12 independent spiked and 12 independent unspiked samples are recorded. The concentration results are analyzed statistically to determine if there is a systematic bias in the method for measuring a particular analyte. If there is a systematic bias, within the limits allowed by Method 301 of this appendix, then a correction factor shall be applied to the analytical results. If the systematic bias is greater than the allowed limits, this method is not valid and cannot be used.

9.2.1 Introduce the spike/tracer gas at a constant flow rate of ≤ 10 percent of the total sample flow, when possible. (Note: Use the rotameter at the end of the sampling train to estimate the required spike/tracer gas flow rate.) Use a flow device, e.g., mass flow meter (± 2 percent), to monitor the spike flow rate. Record the spike flow rate every 10 minutes.

9.2.2 Determine the response time (RT) of the system by continuously collecting spectra of the spiked effluent until the spectrum of the spiked component is constant for 5 minutes. The RT is the interval from the first measurement until the spike becomes constant. Wait for twice the duration of the RT, then collect spectra of two independent spiked gas samples. Duplicate analyses of the spiked concentration shall be within 5 percent of the mean of the two measurements.

9.2.3 Calculate the dilution ratio using the tracer gas as follows:

$$DF = \frac{SF_{6(spk)}}{SF_{6(dir)}} \quad \textbf{(3)}$$

where:

$$CS = DF * Spike_{dir} + Unspike(1-DF) \quad \textbf{(4)}$$

DF = Dilution factor of the spike gas; this value shall be ≥10.

$SF_{6(dir)}$ = $SF_6$ (or tracer gas) concentration measured directly in undiluted spike gas.

$SF_{6(spk)}$ = Diluted $SF_6$ (or tracer gas) concentration measured in a spiked sample.

$Spike_{dir}$ = Concentration of the analyte in the spike standard measured by filling the FTIR cell directly.

CS = Expected concentration of the spiked samples.

Unspike = Native concentration of analytes in unspiked samples

10.0 Calibration and Standardization.

10.1 Signal-to-Noise Ratio (S/N). The RMSD in the noise must be less than one tenth of the minimum analyte peak absorbance in each analytical region. For example if the minimum peak absorbance is 0.01 at the required DL, then RMSD measured over the entire analytical region must be $\leq 0.001$.

10.2 Absorbance Path length. Verify the absorbance path length by comparing reference CTS spectra to test CTS spectra. See appendix E of the FTIR Protocol.

10.3 Instrument Resolution. Measure the line width of appropriate test CTS band(s) to verify instrument resolution. Alternatively, compare CTS spectra to a reference CTS spectrum, if available, measured at the nominal resolution.

10.4 Apodization Function. In transforming the sample interferograms to absorbance spectra use the same

apodization function that was used in transforming the reference spectra.

10.5 FTIR Cell Volume. Evacuate the cell to ≤ 5 mmHg. Measure the initial absolute temperature ($T_i$) and absolute pressure ($P_i$). Connect a wet test meter (or a calibrated dry gas meter), and slowly draw room air into the cell. Measure the meter volume ($V_m$), meter absolute temperature ($T_m$), and meter absolute pressure ($P_m$); and the cell final absolute temperature ($T_f$) and absolute pressure ($P_f$). Calculate the FTIR cell volume $V_{ss}$, including that of the connecting tubing, as follows:

$$V_{SS} = \frac{V_m \frac{P_m}{T_m}}{\left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right]} \quad \textbf{(5)}$$

11.0 Data Analysis and Calculations.

Analyte concentrations shall be measured using reference spectra from the EPA FTIR spectral library. When EPA library spectra are not available, the procedures in section 4.6 of the Protocol shall be followed to prepare reference spectra of all the target analytes.

11.1 Spectral De-resolution. Reference spectra can be converted to lower resolution standard spectra (section 3.3

of this method) by truncating the original reference sample and background interferograms. Appendix K of the FTIR Protocol gives specific deresolution procedures. Deresolved spectra shall be transformed using the same apodization function and level of zero filling as the sample spectra. Additionally, pre-test FTIR protocol calculations (e.g., FRU, MAU, FCU) shall be performed using the de-resolved standard spectra.

11.2 Data Analysis. Various analytical programs are available for relating sample absorbance to a concentration standard. Calculated concentrations shall be verified by analyzing residual baselines after mathematically subtracting scaled reference spectra from the sample spectra. A full description of the data analysis and calculations is contained in the FTIR Protocol (sections 4.0, 5.0, 6.0 and appendices). Correct the calculated concentrations in the sample spectra for differences in absorption path length and temperature between the reference and sample spectra using equation 6,

$$C_{corr} = \left(\frac{L_r}{L_s}\right)\left(\frac{T_s}{T_r}\right)\left(\frac{P_r}{P_s}\right) C_{calc} \qquad \textbf{(6)}$$

where:

$C_{corr}$ = Concentration, corrected for path length.

$C_{calc}$ = Concentration, initial calculation (output of the analytical program designed for the compound).

$L_r$ = Reference spectra path length.

$L_s$ = Sample spectra path length.

$T_s$ = Absolute temperature of the sample gas, K.

$T_r$ = Absolute gas temperature of reference spectra, K.

$P_s$ = Sample cell pressure.

$P_r$ = Reference spectrum sample pressure.

12.0 Method Performance.

12.1 Spectral Quality. Refer to the FTIR Protocol appendices for analytical requirements, evaluation of data quality, and analysis of uncertainty.

12.2 Sampling QA/QC. The analyte spike procedure of section 9 of this method, the QA spike of section 8.6.2 of this method, and the validation procedure of section 13 of this method are used to evaluate the performance of the sampling system and to quantify sampling system effects, if any, on the measured concentrations. This method is self-validating provided that the results meet the performance requirement of the QA spike in sections 9.0 and 8.6.2 of this method and results from a previous method validation study support the use of this method in the application. Several factors can contribute to uncertainty in the measurement of spiked samples. Factors which can be controlled to provide better accuracy in the spiking procedure are listed in sections 12.2.1 through 12.2.4 of this method.

12.2.1 Flow meter. An accurate mass flow meter is accurate to ± 1 percent of its span. If a flow of 1 L/min is monitored with such a MFM, which is calibrated in the range of 0-5 L/min, the flow measurement has an uncertainty of 5 percent. This may be improved by re-calibrating the meter at the specific flow rate to be used.

12.2.2 Calibration gas. Usually the calibration standard is certified to within ± 2 percent. With reactive analytes, such as HCl, the certified accuracy in a commercially available standard may be no better than ± 5 percent.

12.2.3 Temperature. Temperature measurements of the cell shall be quite accurate. If practical, it is preferable to measure sample temperature directly, by inserting a thermocouple into the cell chamber instead of monitoring the cell outer wall temperature.

12.2.4 Pressure. Accuracy depends on the accuracy of the barometer, but fluctuations in pressure throughout a day may be as much as 2.5 percent due to weather variations.

13.0 Method Validation Procedure.

This validation procedure, which is based on EPA Method 301 (40 CFR part 63, appendix A), may be used to validate this method for the analytes in a gas matrix. Validation at one source may also apply to another type of source, if it can be shown that the exhaust gas characteristics are similar at both sources.

13.1 Section 5.3 of Method 301 (40 CFR part 63, appendix A), the Analyte Spike procedure, is used with these modifications. The statistical analysis of the results follows section 6.3 of EPA Method 301. Section 3 of this method defines terms that are not defined in Method 301.

13.1.1 The analyte spike is performed dynamically. This means the spike flow is continuous and constant as spiked samples are measured.

13.1.2 The spike gas is introduced at the back of the sample probe.

13.1.3 Spiked effluent is carried through all sampling components downstream of the probe.

13.1.4 A single FTIR system (or more) may be used to collect and analyze spectra (not quadruplicate integrated sampling trains).

13.1.5 All of the validation measurements are performed sequentially in a single "run" (section 3.26 of this method).

13.1.6 The measurements analyzed statistically are each independent (section 3.22 of this method).

13.1.7 A validation data set can consist of more than 12 spiked and 12 unspiked measurements.

13.2 Batch Sampling. The procedure in sections 13.2.1 through 13.2.2 may be used for stable processes. If process emissions are highly variable, the procedure in section

13.2.3 shall be used.

13.2.1 With a single FTIR instrument and sampling system, begin by collecting spectra of two unspiked samples. Introduce the spike flow into the sampling system and allow 10 cell volumes to purge the sampling system and FTIR cell. Collect spectra of two spiked samples. Turn off the spike and allow 10 cell volumes of unspiked sample to purge the FTIR cell. Repeat this procedure until the 24 (or more) samples are collected.

13.2.2 In batch sampling, collect spectra of 24 distinct samples. (Each distinct sample consists of filling the cell to ambient pressure after the cell has been evacuated.)

13.2.3 Alternatively, a separate probe assembly, line, and sample pump can be used for spiked sample. Verify and document that sampling conditions are the same in both the spiked and the unspiked sampling systems. This can be done by wrapping both sample lines in the same heated bundle. Keep the same flow rate in both sample lines. Measure samples in sequence in pairs. After two spiked samples are measured, evacuate the FTIR cell, and turn the manifold valve so that spiked sample flows to the FTIR cell. Allow the connecting line from the manifold to the FTIR cell to purge thoroughly (the time depends on the line length and flow rate). Collect a pair of spiked samples. Repeat the procedure until at least 24 measurements are completed.

13.3 Simultaneous Measurements With Two FTIR Systems. If unspiked effluent concentrations of the target analyte(s) vary significantly with time, it may be desirable to perform synchronized measurements of spiked and unspiked sample. Use two FTIR systems, each with its own cell and sampling system to perform simultaneous spiked and unspiked measurements. The optical configurations shall be similar, if possible. The sampling configurations shall be the same. One sampling system and FTIR analyzer shall be used to measure spiked effluent. The other sampling system and FTIR analyzer shall be used to measure unspiked flue gas. Both systems shall use the same sampling procedure (i.e., batch or continuous).

13.3.1 If batch sampling is used, synchronize the cell evacuation, cell filling, and collection of spectra. Fill both cells at the same rate (in cell volumes per unit time).

13.3.2 If continuous sampling is used, adjust the sample flow through each gas cell so that the same number of cell volumes pass through each cell in a given time (i.e. $TC_1 = TC_2$).

13.4 Statistical Treatment. The statistical procedure of EPA Method 301 of this appendix, section 6.3 is used to evaluate the bias and precision. For FTIR testing a validation "run" is defined as spectra of 24 independent samples, 12 of which are spiked with the analyte(s) and 12

of which are not spiked.

13.4.1 Bias. Determine the bias (defined by EPA Method 301 of this appendix, section 6.3.2) using equation 7:

$$B = S_m - CS \quad \textbf{(7)}$$

where:

B = Bias at spike level.

$S_m$ = Mean concentration of the analyte spiked samples.

CS = Expected concentration of the spiked samples.

13.4.2 Correction Factor. Use section 6.3.2.2 of Method 301 of this appendix to evaluate the statistical significance of the bias. If it is determined that the bias is significant, then use section 6.3.3 of Method 301 to calculate a correction factor (CF). Analytical results of the test method are multiplied by the correction factor, if $0.7 \leq CF \leq 1.3$. If is determined that the bias is significant and CF > ± 30 percent, then the test method is considered to "not valid."

13.4.3 If measurements do not pass validation, evaluate the sampling system, instrument configuration, and analytical system to determine if improper set-up or a malfunction was the cause. If so, repair the system and repeat the validation.

14.0 Pollution Prevention.

The extracted sample gas is vented outside the enclosure containing the FTIR system and gas manifold after the analysis. In typical method applications the vented sample volume is a small fraction of the source volumetric flow and its composition is identical to that emitted from the source. When analyte spiking is used, spiked pollutants are vented with the extracted sample gas. Approximately 1.6 x $10^{-4}$ to 3.2 x $10^{-4}$ lbs of a single HAP may be vented to the atmosphere in a typical validation run of 3 hours. (This assumes a molar mass of 50 to 100 g, spike rate of 1.0 L/min, and a standard concentration of 100 ppm). Minimize emissions by keeping the spike flow off when not in use.

15.0 Waste Management.

Small volumes of laboratory gas standards can be vented through a laboratory hood. Neat samples must be packed and disposed according to applicable regulations. Surplus materials may be returned to supplier for disposal.

16.0 References.

1. "Field Validation Test Using Fourier Transform Infrared (FTIR) Spectrometry To Measure Formaldehyde, Phenol and Methanol at a Wool Fiberglass Production Facility." Draft. U.S. Environmental Protection Agency Report, EPA Contract No. 68D20163, Work Assignment I-32, September 1994.

2. "FTIR Method Validation at a Coal-Fired Boiler".

Prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No.: EPA-454/R95-004, NTIS No.: PB95-193199. July, 1993.

3. "Method 301 - Field Validation of Pollutant Measurement Methods from Various Waste Media," **40 CFR part 63, appendix A**.

4. "Molecular Vibrations; The Theory of Infrared and Raman Vibrational Spectra," E. Bright Wilson, J. C. Decius, and P. C. Cross, Dover Publications, Inc., 1980. For a less intensive treatment of molecular rotational-vibrational spectra see, for example, "Physical Chemistry," G. M. Barrow, chapters 12, 13, and 14, McGraw Hill, Inc., 1979.

5. "Fourier Transform Infrared Spectrometry," Peter R. Griffiths and James de Haseth, **Chemical Analysis**, **83**, 16-25,(1986), P. J. Elving, J. D. Winefordner and I. M. Kolthoff (ed.), John Wiley and Sons.

6. "Computer-Assisted Quantitative Infrared Spectroscopy," Gregory L. McClure (ed.), **ASTM Special Publication 934** (ASTM), 1987.

7. "Multivariate Least-Squares Methods Applied to the Quantitative Spectral Analysis of Multicomponent Mixtures," **Applied Spectroscopy**, **39**(10), 73-84, 1985.

Table 1. EXAMPLE PRESENTATION OF SAMPLING DOCUMENTATION.

| Sample Time | Spectrum File Name | Background File Name | Sample conditioning | Process condition |
|---|---|---|---|---|
| | | | | |

| Sample Time | Spectrum File | Interferogram | Resolution | Scans | Apodization | Gain | CTS Spectrum |
|---|---|---|---|---|---|---|---|
| | | | | | | | |

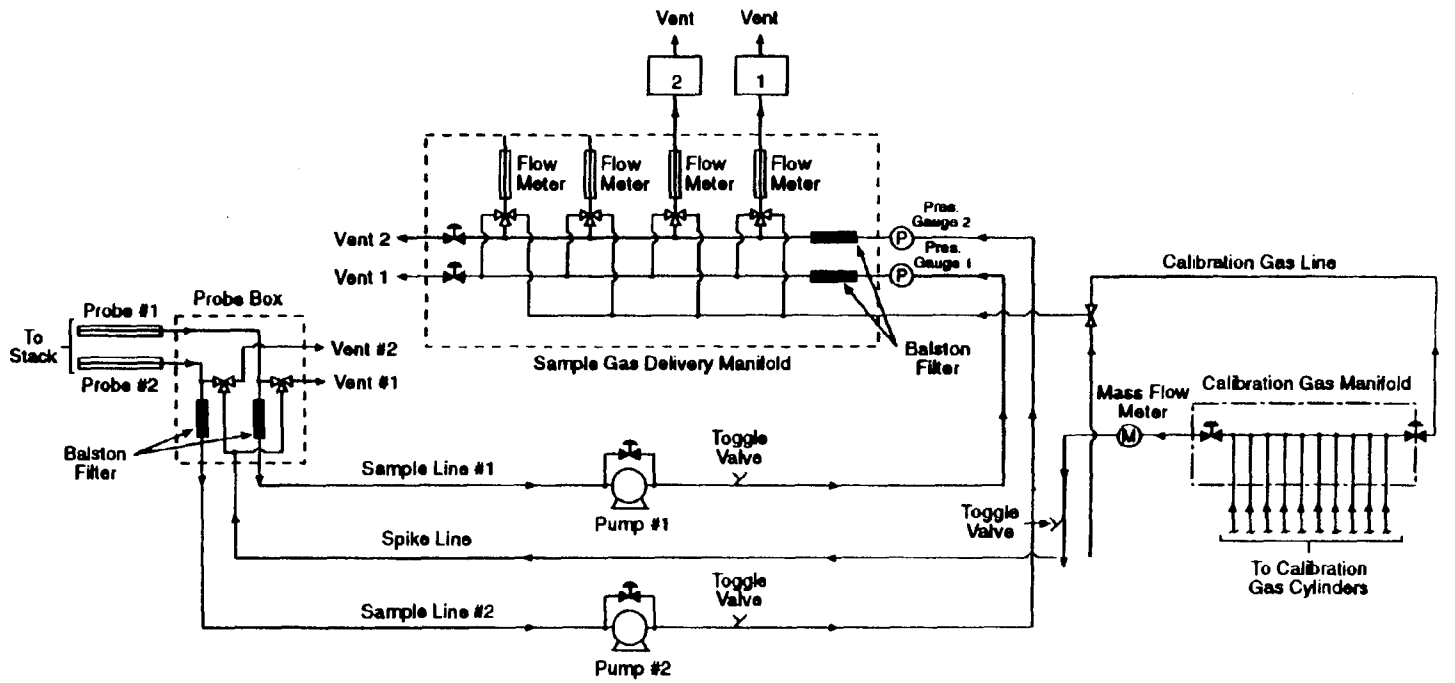



**Figure 1.** Extractive FTIR sampling system.

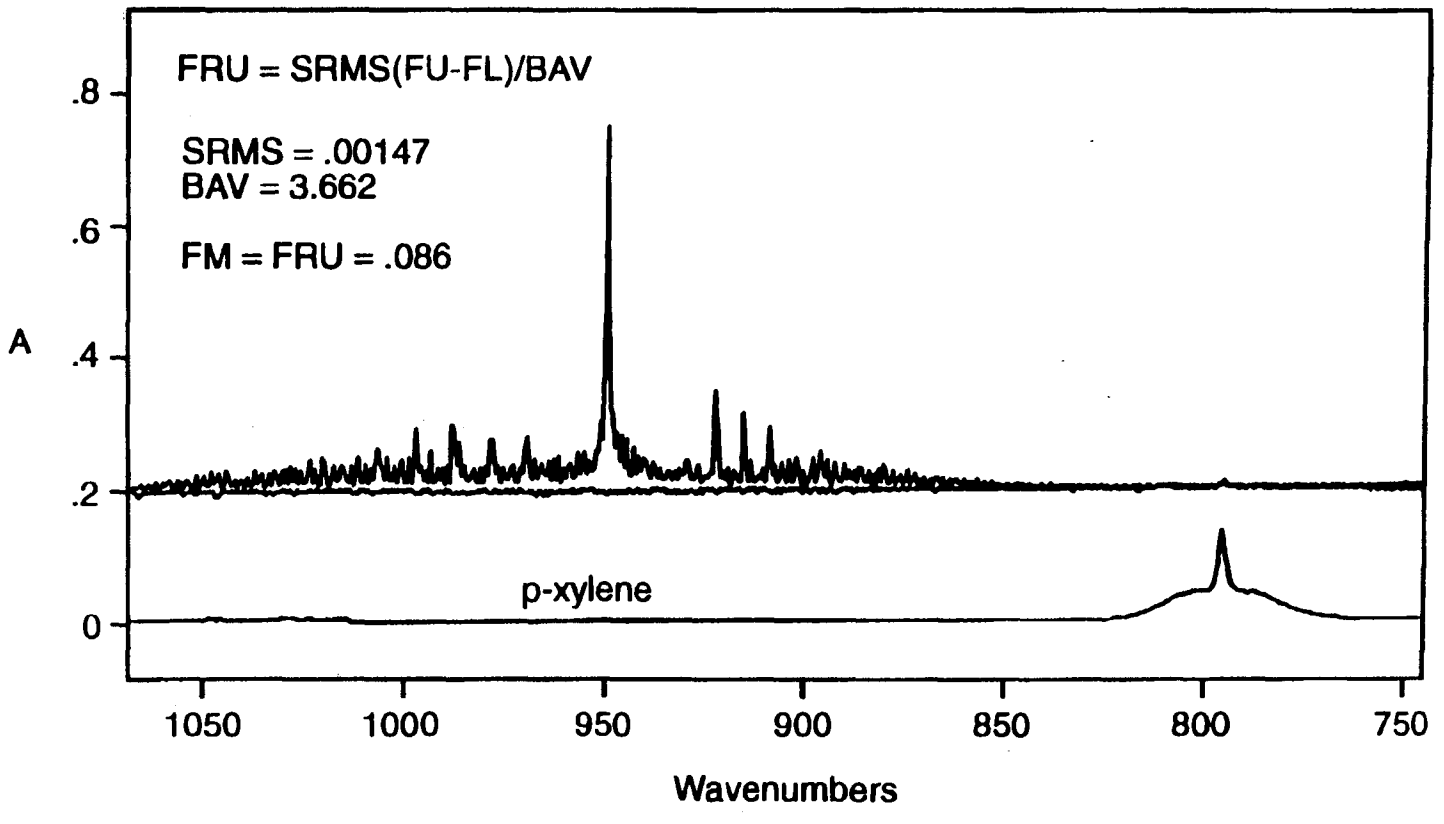



**Figure 2.** Fractional Reproducibility. Top: average of cts1031a and cts1101b. Bottom: Reference spectrum of p-xylene.

# PROTOCOL FOR THE USE OF EXTRACTIVE FOURIER TRANSFORM INFRARED (FTIR) SPECTROMETRY FOR THE ANALYSES OF GASEOUS EMISSIONS FROM STATIONARY SOURCES

## INTRODUCTION

The purpose of this document is to set general guidelines for the use of modern FTIR spectroscopic methods for the analysis of gas samples extracted from the effluent of stationary emission sources. This document outlines techniques for developing and evaluating such methods and sets basic requirements for reporting and quality assurance procedures.

## 1.0 NOMENCLATURE

1.1 Appendix A lists definitions of the symbols and terms used in this Protocol, many of which have been taken directly from American Society for Testing and Materials (ASTM) publication E 131-90a, entitled "Terminology Relating to Molecular Spectroscopy."

1.2 Except in the case of background spectra or where otherwise noted, the term "spectrum" refers to a double-beam spectrum in units of absorbance vs. wavenumber ($cm^{-1}$).

1.3 The term "Study" in this document refers to a publication that has been subjected to EPA- or peer-review.

## 2.0 APPLICABILITY AND ANALYTICAL PRINCIPLE

2.1 Applicability. This Protocol applies to the determination of compound-specific concentrations in single- and multiple-component gas phase samples using double-beam absorption spectroscopy in the mid-infrared band. It does not specifically address other FTIR applications, such as single-beam spectroscopy, analysis of open-path (non-enclosed) samples, and continuous measurement techniques. If multiple spectrometers, absorption cells, or instrumental linewidths are used in such analyses, each distinct operational configuration of the system must be evaluated separately according to this Protocol.

2.2 Analytical Principle.

2.2.1 In the mid-infrared band, most molecules exhibit characteristic gas phase absorption spectra that may be recorded by FTIR systems. Such systems consist of a source of mid-infrared radiation, an interferometer, an enclosed sample cell of known absorption pathlength, an infrared detector, optical elements for the transfer of infrared radiation between components, and gas flow control and measurement components. Adjunct and integral computer systems are used for controlling

the instrument, processing the signal, and for performing both Fourier transforms and quantitative analyses of spectral data.

2.2.2 The absorption spectra of pure gases and of mixtures of gases are described by a linear absorbance theory referred to as Beer's Law. Using this law, modern FTIR systems use computerized analytical programs to quantify compounds by comparing the absorption spectra of known (reference) gas samples to the absorption spectrum of the sample gas. Some standard mathematical techniques used for comparisons are classical least squares, inverse least squares, cross-correlation, factor analysis, and partial least squares. Reference A describes several of these techniques, as well as additional techniques, such as differentiation methods, linear baseline corrections, and non-linear absorbance corrections.

## 3.0 GENERAL PRINCIPLES OF PROTOCOL REQUIREMENTS

The characteristics that distinguish FTIR systems from gas analyzers used in instrumental gas analysis methods (e.g., EPA Methods 6C and 7E) are: (1) Computers are necessary to obtain and analyze data; (2) chemical concentrations can be quantified using previously recorded infrared reference spectra; and (3) analytical assumptions and results, including possible effects of interfering compounds, can be evaluated after the quantitative analysis. The following general principles and requirements of this Protocol are based on these characteristics.

3.1 Verifiability and Reproducibility of Results. Store all data and document data analysis techniques sufficient to allow an independent agent to reproduce the analytical results from the raw interferometric data.

3.2 Transfer of Reference Spectra. To determine whether reference spectra recorded under one set of conditions (e.g., optical bench, instrumental linewidth, absorption pathlength, detector performance, pressure, and temperature) can be used to analyze sample spectra taken under a different set of conditions, quantitatively compare "calibration transfer standards" (CTS) and reference spectra as described in this Protocol. (Note: The CTS may, but need not, include analytes of interest). To effect this, record the absorption spectra of the CTS (a) immediately before and immediately after recording reference spectra and (b) immediately after recording sample spectra.

3.3 Evaluation of FTIR Analyses. The applicability, accuracy, and precision of FTIR measurements are influenced by a number of interrelated factors, which may be divided into two classes:

3.3.1 Sample-Independent Factors. Examples are system configuration and performance (e.g., detector sensitivity and infrared source output), quality and applicability of reference

absorption spectra, and type of mathematical analyses of the spectra. These factors define the fundamental limitations of FTIR measurements for a given system configuration. These limitations may be estimated from evaluations of the system before samples are available. For example, the detection limit for the absorbing compound under a given set of conditions may be estimated from the system noise level and the strength of a particular absorption band. Similarly, the accuracy of measurements may be estimated from the analysis of the reference spectra.

3.3.2 Sample-Dependent Factors. Examples are spectral interferants (e.g., water vapor and $CO_2$) or the overlap of spectral features of different compounds and contamination deposits on reflective surfaces or transmitting windows. To maximize the effectiveness of the mathematical techniques used in spectral analysis, identification of interferants (a standard initial step) and analysis of samples (includes effects of other analytical errors) are necessary. Thus, the Protocol requires post-analysis calculation of measurement concentration uncertainties for the detection of these potential sources of measurement error.

## 4.0 PRE-TEST PREPARATIONS AND EVALUATIONS

Before testing, demonstrate the suitability of FTIR spectrometry for the desired application according to the procedures of this section.

4.1 Identify Test Requirements. Identify and record the test requirements described below in 4.1.1 through 4.1.5. These values set the desired or required goals of the proposed analysis; the description of methods for determining whether these goals are actually met during the analysis comprises the majority of this Protocol.

4.1.1 Analytes (specific chemical species) of interest. Label the analytes from i = 1 to I.

4.1.2 Analytical uncertainty limit ($AU_i$). The $AU_i$ is the maximum permissible fractional uncertainty of analysis for the $i^{th}$ analyte concentration, expressed as a fraction of the analyte concentration in the sample.

4.1.3 Required detection limit for each analyte ($DL_i$, ppm). The detection limit is the lowest concentration of an analyte for which its overall fractional uncertainty ($OFU_i$) is required to be less than its analytical uncertainty limit ($AU_i$).

4.1.4 Maximum expected concentration of each analyte ($CMAX_i$, ppm).

4.2 Identify Potential Interferants. Considering the chemistry of the process or results of previous Studies, identify potential interferants, i.e., the major effluent constituents and any relatively minor effluent constituents that possess either strong absorption characteristics or strong structural similarities to any analyte of interest. Label them 1 through $N_j$, where the subscript "j" pertains to potential interferants. Estimate the concentrations of these compounds in the effluent ($CPOT_j$, ppm).

4.3 Select and Evaluate the Sampling System. Considering the source, e.g., temperature and pressure profiles, moisture content, analyte characteristics, and particulate concentration), select the equipment for extracting gas samples. Recommended are a particulate filter, heating system to maintain sample temperature above the dew point for all sample constituents at all points within the sampling system (including the filter), and sample conditioning system (e.g., coolers, water-permeable membranes that remove water or other compounds from the sample, and dilution devices) to remove spectral interferants or to protect the sampling and analytical components. Determine the minimum absolute sample system pressure ($P_{min}$, mmHg) and the infrared absorption cell volume ($V_{SS}$, liter). Select the techniques and/or equipment for the measurement of sample pressures and temperatures.

4.4 Select Spectroscopic System. Select a spectroscopic configuration for the application. Approximate the absorption pathlength ($L_S'$, meter), sample pressure ($P_S'$, kPa), absolute sample temperature $T_S'$, and signal integration period ($t_{SS}$, seconds) for the analysis. Specify the nominal minimum instrumental linewidth (MIL) of the system. Verify that the fractional error at the approximate values $P_S'$ and $T_S'$ is less than one half the smallest value $AU_i$ (see Section 4.1.2).

4.5 Select Calibration Transfer Standards (CTS's). Select CTS's that meet the criteria listed in Sections 4.5.1, 4.5.2, and 4.5.3.

> Note: It may be necessary to choose preliminary analytical regions (see Section 4.7), identify the minimum analyte linewidths, or estimate the system noise level (see Section 4.12) before selecting the CTS. More than one compound may be needed to meet the criteria; if so, obtain separate cylinders for each compound.

4.5.1 The central wavenumber position of each analytical region lies within 25 percent of the wavenumber position of at least one CTS absorption band.

4.5.2 The absorption bands in 4.5.1 exhibit peak absorbances greater than ten times the value $RMS_{EST}$ (see Section 4.12) but less than 1.5 absorbance units.

4.5.3 At least one absorption CTS band within the operating range of the FTIR instrument has an instrument-independent linewidth no greater than the narrowest analyte absorption band; perform and document measurements or cite Studies to determine analyte and CTS compound linewidths.

4.5.4 For each analytical region, specify the upper and lower wavenumber positions ($FFU_m$ and $FFL_m$, respectively) that bracket the CTS absorption band or bands for the associated analytical region. Specify the wavenumber range, FNU to FNL, containing the absorption band that meets the criterion of Section 4.5.3.

4.5.5 Associate, whenever possible, a single set of CTS gas cylinders with a set of reference spectra. Replacement CTS gas cylinders shall contain the same compounds at concentrations within 5 percent of that of the original CTS cylinders; the entire absorption spectra (not individual spectral segments) of the replacement gas shall be scaled by a factor between 0.95 and 1.05 to match the original CTS spectra.

4.6 Prepare Reference Spectra.

Note: Reference spectra are available in a permanent soft copy from the EPA spectral library on the EMTIC (Emission Measurement Technical Information Center) computer bulletin board; they may be used if applicable.

4.6.1 Select the reference absorption pathlength ($L_R$) of the cell.

4.6.2 Obtain or prepare a set of chemical standards for each analyte, potential and known spectral interferants, and CTS. Select the concentrations of the chemical standards to correspond to the top of the desired range.

4.6.2.1 Commercially-Prepared Chemical Standards. Chemical standards for many compounds may be obtained from independent sources, such as a specialty gas manufacturer, chemical company, or commercial laboratory. These standards (accurate to within ±2 percent) shall be prepared according to EPA Protocol 1 (see Reference D) or shall be traceable to NIST standards. Obtain from the supplier an estimate of the stability of the analyte concentration; obtain and follow all the supplier's recommendations for recertifying the analyte concentration.

4.6.2.2 Self-Prepared Chemical Standards. Chemical standards may be prepared as follows: Dilute certified commercially prepared chemical gases or pure analytes with ultra-pure carrier (UPC) grade nitrogen according to the barometric and volumetric techniques generally described in Reference A, Section A4.6.

4.6.3 Record a set of the absorption spectra of the CTS {R1}, then a set of the reference spectra at two or more concentrations in duplicate over the desired range (the top of the range must be less than 10 times that of the bottom), followed by a second set of CTS spectra {R2}. (If self-prepared standards are used, see Section 4.6.5 before disposing of any of the standards.) The maximum accepted standard concentration-pathlength product (ASCPP) for each compound shall be higher than the maximum estimated concentration-pathlength products for both analytes and known interferants in the effluent gas. For each analyte, the minimum ASCPP shall be no greater than ten times the concentration-pathlength product of that analyte at its required detection limit.

4.6.4 Permanently store the background and interferograms in digitized form. Document details of the mathematical process for generating the spectra from these interferograms. Record the sample pressure ($P_R$), sample temperature ($T_R$), reference absorption pathlength ($L_R$), and interferogram signal integration period ($t_{SR}$). Signal integration periods for the background interferograms shall be $\geq t_{SR}$. Values of $P_R$, $L_R$, and $t_{SR}$ shall not deviate by more than ±1 percent from the time of recording {R1} to that of recording {R2}.

4.6.5 If self-prepared chemical standards are employed and spectra of only two concentrations are recorded for one or more compounds, verify the accuracy of the dilution technique by analyzing the prepared standards for those compounds with a secondary (non-FTIR) technique as follows:

4.6.5.1 Record the response of the secondary technique to each of the four standards prepared.

4.6.5.2 Perform a linear regression of the response values (dependant variable) versus the accepted standard concentration (ASC) values (independent variable), with the regression constrained to pass through the zero-response, zero ASC point.

4.6.5.3 Calculate the average fractional difference between the actual response values and the regression-predicted values (those calculated from the regression line using the four ASC values as the independent variable).

4.6.5.4 If the average fractional difference value calculated in Section 4.6.5.3 is larger for any compound than the corresponding $AU_i$, the dilution technique is not sufficiently accurate and the reference spectra prepared are not valid for the analysis.

4.7 Select Analytical Regions. Using the general considerations in Section 7 of Reference A and the spectral characteristics of the analytes and interferants, select the analytical regions for the application. Label them m = 1 to M. Specify the lower, center and upper wavenumber positions of each

analytical region ($FL_m$, $FC_m$, and $FU_m$, respectively). Specify the analytes and interferants which exhibit absorption in each region.

4.8 Determine Fractional Reproducibility Uncertainties. Using Appendix E, calculate the fractional reproducibility uncertainty for each analyte ($FRU_i$) from a comparison of {R1} and {R2}. If $FRU_i > AU_i$ for any analyte, the reference spectra generated in Section 4.6 are not valid for the application.

4.9 Identify Known Interferants. Using Appendix B, determine which potential interferant affects the analyte concentration determinations. If it does, relabel the potential interferant as "known" interferant, and designate these compounds from k = 1 to K. Appendix B also provides criteria for determining whether the selected analytical regions are suitable.

4.10 Prepare Computerized Analytical Programs.

4.10.1 Choose or devise mathematical techniques (e.g, classical least squares, inverse least squares, cross-correlation, and factor analysis) based on Equation 4 of Reference A that are appropriate for analyzing spectral data by comparison with reference spectra.

4.10.2 Following the general recommendations of Reference A, prepare a computer program or set of programs that analyzes all the analytes and known interferants, based on the selected analytical regions (4.7) and the prepared reference spectra (4.6). Specify the baseline correction technique (e.g., determining the slope and intercept of a linear baseline contribution in each analytical region) for each analytical region, including all relevant wavenumber positions.

4.10.3 Use programs that provide as output [at the reference absorption pathlength ($L_R$), reference gas temperature ($T_R$), and reference gas pressure ($P_R$)] the analyte concentrations, the known interferant concentrations, and the baseline slope and intercept values. If the sample absorption pathlength ($L_S$), sample gas temperature ($T_S$) or sample gas pressure ($P_S$) during the actual sample analyses differ from $L_R$, $T_R$, and $P_R$, use a program or set of programs that applies multiplicative corrections to the derived concentrations to account for these variations, and that provides as output both the corrected and uncorrected values. Include in the report of the analysis (see Section 7.0) the details of any transformations applied to the original reference spectra (e.g., differentiation), in such a fashion that all analytical results may be verified by an independent agent from the reference spectra and data spectra alone.

4.11 Determine the Fractional Calibration Uncertainty. Calculate the fractional calibration uncertainty for each analyte ($FCU_i$) according to Appendix F, and compare these values to the

fractional uncertainty limits ($AU_i$; see Section 4.1). If $FCU_i > AU_i$), either the reference spectra or analytical programs for that analyte are unsuitable.

4.12 Verify System Configuration Suitability. Using Appendix C, measure or obtain estimates of the noise level ($RMS_{EST}$, absorbance) of the FTIR system; alternatively, construct the complete spectrometer system and determine the values $RMS_{Sm}$ using Appendix G. Estimate the minimum measurement uncertainty for each analyte ($MAU_i$, ppm) and known interferant ($MIU_k$, ppm) using Appendix D. Verify that (a) $MAU_i < (AU_i)(DL_i)$, $FRU_i < AU_i$, and $FCU_i < AU_i$ for each analyte and that (b) the CTS chosen meets the requirements listed in Section 4.5.

## 5.0 SAMPLING AND ANALYSIS PROCEDURE

5.1 Analysis System Assembly and Leak-Test. Assemble the analysis system. Allow sufficient time for all system components to reach the desired temperature. Then determine the leak-rate ($L_R$) and leak volume ($V_L$), where $V_L = L_R\ t_{SS}$. Leak volumes shall be ≤4 percent of $V_{SS}$.

5.2 Verify Instrumental Performance. Measure the noise level of the system in each analytical region using the procedure of Appendix G. If any noise level is higher than that estimated for the system in Section 4.12, repeat the calculations of Appendix D and verify that the requirements of Section 4.12 are met; if they are not, adjust or repair the instrument and repeat this section.

5.3 Determine the Sample Absorption Pathlength. Record a background spectrum. Then, fill the absorption cell with CTS at the pressure $P_R$ and record a set of CTS spectra {R3}. Store the background and unscaled CTS single beam interferograms and spectra. Using Appendix H, calculate the sample absorption pathlength ($L_S$) for each analytical region. The values $L_S$ shall not differ from the approximated sample pathlength $L_S'$ (see Section 4.4) by more than 5 percent.

5.4 Record Sample Spectrum. Connect the sample line to the source. Either evacuate the absorption cell to an absolute pressure below 5 mmHg before extracting a sample from the effluent stream into the absorption cell, or pump at least ten cell volumes of sample through the cell before obtaining a sample. Record the sample pressure $P_S$. Generate the absorbance spectrum of the sample. Store the background and sample single beam interferograms, and document the process by which the absorbance spectra are generated from these data. (If necessary, apply the spectral transformations developed in Section 5.6.2). The resulting sample spectrum is referred to below as $S_S$.

Note: Multiple sample spectra may be recorded according to the procedures of Section 5.4 before performing Sections 5.5 and 5.6.

5.5 Quantify Analyte Concentrations. Calculate the unscaled analyte concentrations $RUA_i$ and unscaled interferant concentrations $RUI_K$ using the programs developed in Section 4. To correct for pathlength and pressure variations between the reference and sample spectra, calculate the scaling factor $R_{LPS} = (L_R P_R T_S)/(L_S P_S T_R)$. Calculate the final analyte and interferant concentrations $RSA_i = R_{LPS} RUA_i$ and $RSI_k = R_{LPS} RUI_k$.

5.6 Determine Fractional Analysis Uncertainty. Fill the absorption cell with CTS at the pressure $P_S$. Record a set of CTS spectra {R4}. Store the background and CTS single beam interferograms. Using Appendix H, calculate the fractional analysis uncertainty (FAU) for each analytical region. If the FAU indicated for any analytical region is larger than the required accuracy requirements determined in Section 4.1, then comparisons to previously recorded reference spectra are invalid in that analytical region, and the analyst shall perform one or both of the following procedures:

5.6.1 Perform instrumental checks and adjust the instrument to restore its performance to acceptable levels. If adjustments are made, repeat Sections 5.3, 5.4 (except for the recording of a sample spectrum), and 5.5 to demonstrate that acceptable uncertainties are obtained in all analytical regions.

5.6.2 Apply appropriate mathematical transformations (e.g., frequency shifting, zero-filling, apodization, smoothing) to the spectra (or to the interferograms upon which the spectra are based) generated during the performance of the procedures of Section 5.3. Document these transformations and their reproducibility. Do not apply multiplicative scaling of the spectra, or any set of transformations that is mathematically equivalent to multiplicative scaling. Different transformations may be applied to different analytical regions. Frequency shifts shall be smaller than one-half the minimum instrumental linewidth, and must be applied to all spectral data points in an analytical region. The mathematical transformations may be retained for the analysis if they are also applied to the appropriate analytical regions of all sample spectra recorded, and if all original sample spectra are digitally stored. Repeat Sections 5.3, 5.4 (except the recording of a sample spectrum), and 5.5 to demonstrate that these transformations lead to acceptable calculated concentration uncertainties in all analytical regions.

## 6.0 POST-ANALYSIS EVALUATIONS

Estimate the overall accuracy of the analyses performed in Section 5 as follows:

6.1 Qualitatively Confirm the Assumed Matrix. Examine each analytical region of the sample spectrum for spectral evidence of unexpected or unidentified interferants. If found, identify the interfering compounds (see Reference C for guidance) and add them to the list of known interferants. Repeat the procedures of Section 4 to include the interferants in the uncertainty calculations and analysis procedures. Verify that the MAU and FCU values do not increase beyond acceptable levels for the application requirements. Re-calculate the analyte concentrations (Section 5.5) in the affected analytical regions.

6.2 Quantitatively Evaluate Fractional Model Uncertainty (FMU). Perform the procedures of either Section 6.2.1 or 6.2.2:

6.2.1 Using Appendix I, determine the fractional model error (FMU) for each analyte.

6.2.2 Provide statistically determined uncertainties FMU for each analyte which are equivalent to two standard deviations at the 95% confidence level. Such determinations, if employed, must be based on mathematical examinations of the pertinent sample spectra (not the reference spectra alone). Include in the report of the analysis (see Section 7.0) a complete description of the determination of the concentration uncertainties.

6.3 Estimate Overall Concentration Uncertainty (OCU). Using Appendix J, determine the overall concentration uncertainty (OCU) for each analyte. If the OCU is larger than the required accuracy for any analyte, repeat Sections 4 and 6.

## 7.0 REPORTING REQUIREMENTS

**[Documentation pertaining to virtually all the procedures of Sections 4, 5, and 6 will be required. Software copies of reference spectra and sample spectra will be retained for some minimum time following the actual testing.]**

## 8.0 REFERENCES

A) Standard Practices for General Techniques of Infrared Quantitative Analysis (American Society for Testing and Materials, Designation E 168-88).

B) The Coblentz Society Specifications for Evaluation of Research Quality Analytical Infrared Reference Spectra (Class II); Anal. Chemistry 47, 945A (1975); **Appl. Spectroscopy 444, pp. 211-215, 1990.**

C) Standard Practices for General Techniques for Qualitative Infrared Analysis, American Society for Testing and Materials, Designation E 1252-88.

D) "Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Continuous Emissions Monitors (Protocol Number 1)," June 1978, Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods, EPA-600/4-77-027b, August 1977.

## APPENDIX A

DEFINITIONS OF TERMS AND SYMBOLS

### A.1 Definitions of Terms

**absorption band** - a contiguous wavenumber region of a spectrum (equivalently, a contiguous set of absorbance spectrum data points) in which the absorbance passes through a maximum or a series of maxima.

**absorption pathlength** - in a spectrophotometer, the distance, measured in the direction of propagation of the beam of radiant energy, between the surface of the specimen on which the radiant energy is incident and the surface of the specimen from which it is emergent.

**analytical region** - a contiguous wavenumber region (equivalently, a contiguous set of absorbance spectrum data points) used in the quantitative analysis for one or more analyte.

Note: The quantitative result for a single analyte may be based on data from more than one analytical region.

**apodization** - modification of the ILS function by multiplying the

interferogram by a weighing function whose magnitude varies with retardation.

**background spectrum** - the single beam spectrum obtained with all system components without sample present.

**baseline** - any line drawn on an absorption spectrum to establish a reference point that represents a function of the radiant power incident on a sample at a given wavelength.

**Beers's law** - the direct proportionality of the absorbance of a compound in a homogeneous sample to its concentration.

**calibration transfer standard (CTS) gas** - a gas standard of a compound used to achieve and/or demonstrate suitable quantitative agreement between sample spectra and the reference spectra; see Section 4.5.1.

**compound** - a substance possessing a distinct, unique molecular structure.

**concentration (c)** - the quantity of a compound contained in a unit quantity of sample. The unit "ppm" (number, or mole, basis) is recommended.

**concentration-pathlength product** - the mathematical product of concentration of the species and absorption pathlength. For

reference spectra, this is a known quantity; for sample spectra, it is the quantity directly determined from Beer's law. The units "centimeters-ppm" or "meters-ppm" are recommended.

**derivative absorption spectrum** - a plot of rate of change of absorbance or of any function of absorbance with respect to wavelength or any function of wavelength.

**double beam spectrum** - a transmission or absorbance spectrum derived by dividing the sample single beam spectrum by the background spectrum.

Note: The term "double-beam" is used elsewhere to denote a spectrum in which the sample and background interferograms are collected simultaneously along physically distinct absorption paths. Here, the term denotes a spectrum in which the sample and background interferograms are collected at different times along the same absorption path.

**fast Fourier transform (FFT)** - a method of speeding up the computation of a discrete FT by factoring the data into sparse matrices containing mostly zeros.

**flyback** - interferometer motion during which no data are recorded.

**Fourier transform (FT)** - the mathematical process for converting an amplitude-time spectrum to an amplitude-frequency spectrum, or vice versa.

**Fourier transform infrared (FTIR) spectrometer** - an analytical system that employs a source of mid-infrared radiation, an interferometer, an enclosed sample cell of known absorption pathlength, an infrared detector, optical elements that transfer infrared radiation between components, and a computer system. The time-domain detector response (interferogram) is processed by a Fourier transform to yield a representation of the detector response vs. infrared frequency.

Note: When FTIR spectrometers are interfaced with other instruments, a slash should be used to denote the interface; e.g., GC/FTIR; HPCL/FTIR, and the use of FTIR should be explicit; i.e., FTIR not IR.

**frequency, $\nu$** - the number of cycles per unit time.

**infrared** - the portion of the electromagnetic spectrum containing wavelengths from approximately 0.78 to 800 microns.

**interferogram, $I(\sigma)$** - record of the modulated component of the interference signal measured as a function of retardation by the detector.

**interferometer** - device that divides a beam of radiant energy into two or more paths, generate an optical path difference between the beams, and recombines them in order to produce repetitive interference maxima and minima as the optical retardation is varied.

**linewidth** - the full width at half maximum of an absorption band in units of wavenumbers ($cm^{-1}$).

**mid-infrared** - the region of the electromagnetic spectrum from approximately 400 to 5000 $cm^{-1}$.

**pathlength** - see "absorption pathlength."

**reference spectra** - absorption spectra of gases with known chemical compositions, recorded at a known absorption pathlength, which are used in the quantitative analysis of gas samples.

**retardation,** $\sigma$ - optical path difference between two beams in an interferometer; also known as "optical path difference" or "optical retardation."

**scan** - digital representation of the detector output obtained during one complete motion of the interferometer's moving assembly or assemblies.

**scaling** - application of a multiplicative factor to the absorbance values in a spectrum.

**single beam spectrum** - Fourier-transformed interferogram, representing the detector response vs. wavenumber.

Note: The term "single-beam" is used elsewhere to denote any spectrum in which the sample and background interferograms are recorded on the same physical absorption path; such usage differentiates such spectra from those generated using interferograms recorded along two physically distinct absorption paths (see "double-beam spectrum" above). Here, the term applies (for example) to the two spectra used directly in the calculation of transmission and absorbance spectra of a sample.

**standard reference material** - a reference material, the composition or properties of which are certified by a recognized standardizing agency or group.

Note: The equivalent ISO term is "certified reference material."

**transmittance,** $T$ - the ratio of radiant power transmitted by the sample to the radiant power incident on the sample. Estimated in FTIR spectroscopy by forming the ratio of the single-beam sample and background spectra.

**wavenumber**, $\bar{\nu}$ - the number of waves per unit length.

Note: The usual unit of wavenumber is the reciprocal centimeter, $cm^{-1}$. The wavenumber is the reciprocal of the wavelength, $\lambda$, when $\lambda$ is expressed in centimeters.

**zero-filling** - the addition of zero-valued points to the end of a measured interferogram.

Note: Performing the FT of a zero-filled interferogram results in correctly interpolated points in the computed spectrum.

## A.2 Definitions of Mathematical Symbols

**A, absorbance** - the logarithm to the base 10 of the reciprocal of the transmittance (T).

$$A = \log_{10}\left(\frac{1}{T}\right) = -\log_{10}T \qquad (1)$$

**$AAI_{im}$** - band area of the $i^{th}$ analyte in the $m^{th}$ analytical region, at the concentration ($CL_i$) corresponding to the product of its required detection limit ($DL_i$) and analytical uncertainty limit ($AU_i$) .

**$AAV_{im}$** - average absorbance of the $i^{th}$ analyte in the $m^{th}$ analytical region, at the concentration ($CL_i$) corresponding to the product of its required detection limit ($DL_i$) and analytical uncertainty limit ($AU_i$) .

**ASC, accepted standard concentration** - the concentration value assigned to a chemical standard.

**ASCPP, accepted standard concentration-pathlength product** - for a chemical standard, the product of the ASC and the sample absorption pathlength. The units "centimeters-ppm" or "meters-ppm" are recommended.

**$AU_i$, analytical uncertainty limit** - the maximum permissible fractional uncertainty of analysis for the $i^{th}$ analyte concentration, expressed as a fraction of the analyte concentration determined in the analysis.

**$AVT_m$** - average estimated total absorbance in the $m^{th}$ analytical region.

**$CKWN_k$** - estimated concentration of the $k^{th}$ known interferant.

**$CMAX_i$** - estimated maximum concentration of the $i^{th}$ analyte.

$CPOT_j$ - estimated concentration of the $j^{th}$ potential interferant.

$DL_i$, **required detection limit** - for the $i^{th}$ analyte, the lowest concentration of the analyte for which its overall fractional uncertainty ($OFU_i$) is required to be less than the analytical uncertainty limit ($AU_i$).

$FC_m$ - center wavenumber position of the $m^{th}$ analytical region.

$FAU_i$, **fractional analytical uncertainty** - calculated uncertainty in the measured concentration of the $i^{th}$ analyte because of errors in the mathematical comparison of reference and sample spectra.

$FCU_i$, **fractional calibration uncertainty** - calculated uncertainty in the measured concentration of the $i^{th}$ analyte because of errors in Beer's law modeling of the reference spectra concentrations.

$FFL_m$ - lower wavenumber position of the CTS absorption band associated with the $m^{th}$ analytical region.

$FFU_m$ - upper wavenumber position of the CTS absorption band associated with the $m^{th}$ analytical region.

$FL_m$ - lower wavenumber position of the $m^{th}$ analytical region.

$FMU_i$, **fractional model uncertainty** - calculated uncertainty in the measured concentration of the $i^{th}$ analyte because of errors in the absorption model employed.

$FN_L$ - lower wavenumber position of the CTS spectrum containing an absorption band at least as narrow as the analyte absorption bands.

$FN_U$ - upper wavenumber position of the CTS spectrum containing an absorption band at least as narrow as the analyte absorption bands.

$FRU_i$, **fractional reproducibility uncertainty** - calculated uncertainty in the measured concentration of the $i^{th}$ analyte because of errors in the reproducibility of spectra from the FTIR system.

$FU_m$ - upper wavenumber position of the $m^{th}$ analytical region.

$IAI_{jm}$ - band area of the $j^{th}$ potential interferant in the $m^{th}$ analytical region, at its expected concentration ($CPOT_j$).

$IAV_{im}$ - average absorbance of the $i^{th}$ analyte in the $m^{th}$ analytical region, at its expected concentration ($CPOT_j$).

**$ISC_{i \text{ or } k}$, indicated standard concentration** - the concentration from the computerized analytical program for a single-compound reference spectrum for the $i^{th}$ analyte or $k^{th}$ known interferant.

**kPa** - kilo-Pascal (see Pascal).

**$L_S'$** - estimated sample absorption pathlength.

**$L_R$** - reference absorption pathlength.

**$L_S$** - actual sample absorption pathlength.

**$MAU_i$** - mean of the $MAU_{im}$ over the appropriate analytical regions.

**$MAU_{im}$, minimum analyte uncertainty** - the calculated minimum concentration for which the analytical uncertainty limit ($AU_i$) in the measurement of the $i^{th}$ analyte, based on spectral data in the $m^{th}$ analytical region, can be maintained.

**$MIU_j$** - mean of the $MIU_{jm}$ over the appropriate analytical regions.

**$MIU_{jm}$, minimum interferant uncertainty** - the calculated minimum concentration for which the analytical uncertainty limit $CPOT_j/20$ in the measurement of the $j^{th}$ interferant, based on spectral data in the $m^{th}$ analytical region, can be maintained.

**MIL, minimum instrumental linewidth** - the minimum linewidth from the FTIR system, in wavenumbers.

Note: The MIL of a system may be determined by observing an absorption band known (through higher resolution examinations) to be narrower than indicated by the system. The MIL is fundamentally limited by the retardation of the interferometer, but is also affected by other operational parameters (e.g., the choice of apodization).

**$N_i$** - number of analytes.

**$N_j$** - number of potential interferants.

**$N_k$** - number of known interferants.

**$N_{scan}$** - the number of scans averaged to obtain an interferogram.

**$OFU_i$** - the overall fractional uncertainty in an analyte concentration determined in the analysis ($OFU_i = MAX\{FRU_i, FCU_i, FAU_i, FMU_i\}$).

**Pascal (Pa)** - metric unit of static pressure, equal to one Newton per square meter; one atmosphere is equal to 101,325 Pa;

1/760 atmosphere (one Torr, or one millimeter Hg) is equal to 133.322 Pa.

$P_{min}$ - minimum pressure of the sampling system during the sampling procedure.

$P_S'$ - estimated sample pressure.

$P_R$ - reference pressure.

$P_S$ - actual sample pressure.

$RMS_{Sm}$ - measured noise level of the FTIR system in the $m^{th}$ analytical region.

**RMSD, root mean square difference** - a measure of accuracy determined by the following equation:

$$RMSD = \sqrt{\left(\frac{1}{n}\right) \sum_{i=1}^{n} e_i^2} \qquad (2)$$

where:

n = the number of observations for which the accuracy is determined.

$e_i$ = the difference between a measured value of a property and its mean value over the n observations.

Note: The RMSD value "between a set of n contiguous absorbance values ($A_i$) and the mean of the values" ($A_M$) is defined as

$$RMSD = \sqrt{\left(\frac{1}{n}\right) \sum_{i=1}^{n} (A_i - A_M)^2} \qquad (3)$$

$RSA_i$ - the (calculated) final concentration of the $i^{th}$ analyte.

$RSI_k$ - the (calculated) final concentration of the $k^{th}$ known interferant.

$t_{scan}$, **scan time** - time used to acquire a single scan, not including flyback.

$t_S$, **signal integration period** - the period of time over which an interferogram is averaged by addition and scaling of individual scans. In terms of the number of scans $N_{scan}$ and scan time $t_{scan}$, $t_S = N_{scan} t_{scan}$.

$t_{SR}$ - signal integration period used in recording reference spectra.

$t_{SS}$ - signal integration period used in recording sample spectra.

$T_R$ - absolute temperature of gases used in recording reference spectra.

$T_S$ - absolute temperature of sample gas as sample spectra are recorded.

**TP, Throughput** - manufacturer's estimate of the fraction of the total infrared power transmitted by the absorption cell and transfer optics from the interferometer to the detector.

$V_{SS}$ - volume of the infrared absorption cell, including parts of attached tubing.

$W_{ik}$ - weight used to average over analytical regions k for quantities related to the analyte i; see Appendix D.

Note that some terms are missing, e.g., $BAV_m$, OCU, $RMSS_m$, $SUB_S$, $SIC_i$, $SAC_i$, $S_S$

## APPENDIX B

IDENTIFYING SPECTRAL INTERFERANTS

### B.1 General

B.1.1 Assume a fixed absorption pathlength equal to the value $L_S'$.

B.1.2 Use band area calculations to compare the relative absorption strengths of the analytes and potential interferants. In the $m^{th}$ analytical region ($FL_m$ to $FU_m$), use either rectangular or trapezoidal approximations to determine the band areas described below (see Reference A, Sections A.3.1 through A.3.3); document any baseline corrections applied to the spectra.

B.1.3 Use the average total absorbance of the analytes and potential interferants in each analytical region to determine whether the analytical region is suitable for analyte concentration determinations.

> Note: The average absorbance in an analytical region is the band area divided by the width of the analytical region in wavenumbers. The average total absorbance in an analytical region is the sum of the average absorbances of all analytes and potential interferants.

### B.2 Calculations

B.2.1 Prepare spectral representations of each analyte at the concentration $CL_i = (DL_i)(AU_i)$, where $DL_i$ is the required detection limit and $AU_i$ is the maximum permissible analytical uncertainty. For the $m^{th}$ analytical region, calculate the band area ($AAI_{im}$) and average absorbance ($AAV_{im}$) from these scaled analyte spectra.

B.2.2 Prepare spectral representations of each potential interferant at its expected concentration ($CPOT_j$). For the $m^{th}$ analytical region, calculate the band area ($IAI_{jm}$) and average absorbance ($IAV_{jm}$) from these scaled potential interferant spectra.

B.2.3 Repeat the calculation for each analytical region, and record the band area results in matrix form as indicated in Figure B.1.

B.2.4 If the band area of any potential interferant in an analytical region is greater than the one-half the band area of any analyte (i.e., $IAI_{jm} > 0.5\ AAI_{im}$ for any pair ij and any m), classify the potential interferant as known interferant. Label the known interferants k = 1 to K. Record the results in matrix form as indicated in Figure B.2.

B.2.5 Calculate the average total absorbance ($AVT_m$) for each analytical region and record the values in the last row of the matrix described in Figure B.2. Any analytical region where $AVT_m$ >2.0 is unsuitable.

FIGURE B.1 Presentation of Potential Interferant Calculations

| | Analytical Regions 1 . . . . . M |
|---|---|
| Analyte Labels | |
| 1 | $AAI_{11}$ . . . $AAI_{1M}$ |
| . | . . |
| . | . . |
| I | $AAI_{I1}$ . . . $AAI_{IM}$ |
| Potential Interferant Labels | |
| 1 | $IAI_{11}$ . . . $IAI_{1M}$ |
| . | . . |
| . | . . |
| J | $IAI_{J1}$ . . . $IAI_{JM}$ |

FIGURE B.2 Presentation of Known Interferant Calculations

| | Analytical Regions 1 . . . . . M |
|---|---|
| Analyte Labels | |
| 1 | $AAI_{11}$ . . . . $AAI_{1M}$ |
| . | . . |
| . | . . |
| I | $AAI_{I1}$ . . . . $AAI_{IM}$ |
| Known Interferant Labels | |
| 1 | $IAI_{11}$ . . . . $IAI_{1M}$ |
| . | . . |
| . | . . |
| K | $IAI_{K1}$ . . . . $IAI_{KM}$ |
| Total Average Absorbance | $AVT_1$ $AVT_M$ |

## APPENDIX C

ESTIMATING NOISE LEVELS

### C.1 General

C.1.1 The root-mean-square (RMS) noise level is the standard measure of noise in this Protocol. The RMS noise level of a contiguous segment of a spectrum is defined as the RMS difference (RMSD) between the absorbance values which form the segment and the mean value of that segment (see Appendix A).

C.1.2 The RMS noise value in double-beam absorbance spectra is assumed to be inversely proportional to: (a) the square root of the signal integration period of the sample single beam spectra from which it is formed, and (b) to the total infrared power transmitted through the interferometer and absorption cell.

C.1.3 Practically, the assumption of C.1.2 allow the RMS noise level of a complete system to be estimated from the following four quantities:

(a) $RMS_{MAN}$ - the noise level of the system (in absorbance units), without the absorption cell and transfer optics, under those conditions necessary to yield the specified minimum instrumental linewidth, e.g., Jacquinot stop size.

(b) $t_{MAN}$ - the manufacturer's signal integration time used to determine $RMS_{MAN}$.

(c) $t_{SS}$ - the signal integration time for the analyses.

(d) TP - the manufacturer's estimate of the fraction of the total infrared power transmitted by the absorption cell and transfer optics from the interferometer to the detector.

### C.2 Calculations

C.2.1 Obtain the values of $RMS_{MAN}$, $t_{MAN}$, and TP from the manufacturers of the equipment, or determine the noise level by direct measurements with the completely constructed system proposed in Section 4.

C.2.2 Calculate the noise value of the system ($RMS_{EST}$) as follows:

$$RMS_{EST} = RMS_{MAN} \; TP \sqrt{\frac{t_{ss}}{t_{MAN}}} \qquad (4)$$

## APPENDIX D

ESTIMATING MINIMUM CONCENTRATION MEASUREMENT UNCERTAINTIES (MAU and MIU)

### D.1 General

Estimate the minimum concentration measurement uncertainties for the $i^{th}$ analyte ($MAU_i$) and $j^{th}$ interferant ($MIU_j$) based on the spectral data in the $m^{th}$ analytical region by comparing the analyte band area in the analytical region ($AAI_{im}$) and estimating or measuring the noise level of the system ($RMS_{EST}$ or $RMS_{Sm}$).

Note: For a single analytical region, the MAU or MIU value is the concentration of the analyte or interferant for which the band area is equal to the product of the analytical region width (in wavenumbers) and the noise level of the system (in absorbance units). If data from more than one analytical region is used in the determination of an analyte concentration, the MAU or MIU is the mean of the separate MAU or MIU values calculated for each analytical region.

### D.2 Calculations

D.2.1 For each analytical region, set RMS = $RMS_{Sm}$ if measured (Appendix G), or set RMS = $RMS_{EST}$ if estimated (Appendix C).

D.2.2 For each analyte associated with the analytical region, calculate

$$MAU_{im} = (RMS)(DL_i)(AU_i)\frac{(FU_m - FL_m)}{AAI_{im}} \quad (5)$$

D.2.3 If only the $m^{th}$ analytical region is used to calculate the concentration of the $i^{th}$ analyte, set $MAU_i = MAU_{im}$.

D.2.4 If a number of analytical regions are used to calculate the concentration of the $i^{th}$ analyte, set $MAU_i$ equal to the weighted mean of the appropriate $MAU_{im}$ values calculated above; the weight for each term in the mean is equal to the fraction of the total wavenumber range used for the calculation represented by each analytical region. Mathematically, if the set of analytical regions employed is {m'}, then the MAU for each analytical region is

$$MAU_i = \sum_{k \in (m')} W_{ik} \; MAU_{ik} \qquad (6)$$

where the weight $W_{ik}$ is defined for each term in the sum as

$$W_{ik} = ( FM_k - FL_k ) \left( \sum_{p \in (m')} [FM_p - FL_p] \right)^{-1} \qquad (7)$$

D.2.5 Repeat Sections D.2.1 through D.2.4 to calculate the analogous values $MIU_j$ for the interferants j = 1 to J. Replace the value $(AU_i)(DL_i)$ in the above equations with $CPOT_j/20$; replace the value $AAI_{im}$ in the above equations with $IAI_{jm}$.

## APPENDIX E

DETERMINING FRACTIONAL REPRODUCIBILITY UNCERTAINTIES (FRU)

### E.1 General

To estimate the reproducibility of the spectroscopic results of the system, compare the CTS spectra recorded before and after preparing the reference spectra. Compare the difference between the spectra to their average band area. Perform the calculation for each analytical region on the portions of the CTS spectra associated with that analytical region.

### E.2 Calculations

E.2.1 The CTS spectra {R1} consist of N spectra, denoted by $S_{1i}$, i=1, N. Similarly, the CTS spectra {R2} consist of N spectra, denoted by $S_{2i}$, i=1, N. Each $S_{ki}$ is the spectrum of a single compound, where i denotes the compound and k denotes the set {Rk} of which $S_{ki}$ is a member. Form the spectra $S_3$ according to $S_{3i} = S_{2i}-S_{1i}$ for each i. Form the spectra $S_4$ according to $S_{4i} = [S_{2i}+S_{1i}]/2$ for each i.

E.2.2 Each analytical region m is associated with a portion of the CTS spectra $S_{2i}$ and $S_{1i}$, for a particular i, with lower and upper wavenumber limits $FFL_m$ and $FFU_m$, respectively.

E.2.3 For each m and the associated i, calculate the band area of $S_{4i}$ in the wavenumber range $FFU_m$ to $FFL_m$. Follow the guidelines of Section B.1.2 for this band area calculation. Denote the result by $BAV_m$.

E.2.4 For each m and the associated i, calculate the RMSD of $S_{3i}$ between the absorbance values and their mean in the wavenumber range $FFU_m$ to $FFL_m$. Denote the result by $SRMS_m$.

E.2.5 For each analytical region m, calculate the quantity

$$FM_m = SRMS_m(FFU_m-FFL_m)/BAV_m$$

E.2.6 If only the $m^{th}$ analytical region is used to calculate the concentration of the $i^{th}$ analyte, set $FRU_i = FM_m$.

E.2.7 If a number $p_i$ of analytical regions are used to calculate the concentration of the $i^{th}$ analyte, set $FRU_i$ equal to the weighted mean of the appropriate $FM_m$ values calculated above. Mathematically, if the set of analytical regions employed is {m'}, then

$$FRU_i = \sum_{k \in \{m'\}} W_{ik} FM_k \qquad (8)$$

where the $W_{ik}$ are calculated as described in Appendix D.

## APPENDIX F

DETERMINING FRACTIONAL CALIBRATION UNCERTAINTIES (FCU)

### F.1 General

F.1.1 The concentrations yielded by the computerized analytical program applied to each single-compound reference spectrum are defined as the indicated standard concentrations (ISC's). The ISC values for a single compound spectrum should ideally equal the accepted standard concentration (ASC) for one analyte or interferant, and should ideally be zero for all other compounds. Variations from these results are caused by errors in the ASC values, variations from the Beer's law (or modified Beer's law) model used to determine the concentrations, and noise in the spectra. When the first two effects dominate, the systematic nature of the errors is often apparent; take steps to correct them.

F.1.2 When the calibration error appears non-systematic, apply the following method to estimate the fractional calibration uncertainty (FCU) for each compound. The FCU is defined as the mean fractional error between the ASC and the ISC for all reference spectra with non-zero ASC for that compound. The FCU for each compound shall be less than the required fractional uncertainty specified in Section 4.1.

F.1.3 The computerized analytical programs shall also be required to yield acceptably low concentrations for compounds with ISC=0 when applied to the reference spectra. The limits chosen in this Protocol are that the ISC of each reference spectrum for each analyte or interferant shall not exceed that compound's minimum measurement uncertainty (MAU or MIU).

### F.2 Calculations

F.2.1 Apply each analytical program to each reference spectrum. Prepare a similar table as that in Figure F.1 to present the ISC and ASC values for each analyte and interferant in each reference spectrum. Maintain the order of reference file names and compounds employed in preparing Figure F.1.

F.2.2 For all reference spectra in Figure F.1, verify that the absolute value of the ISC's are less than the compound's MAU (for analytes) or MIU (for interferants).

F.2.3 For each analyte reference spectrum, calculate the quantity (ASC-ISC)/ASC. For each analyte, calculate the mean of these values (the $FCU_i$ for the $i^{th}$ analyte) over all reference spectra. Prepare a similar table as that in Figure F.2 to present the $FCU_i$ and analytical uncertainty limit ($AU_i$) for each analyte.

FIGURE F.1

Presentation of Accepted Standard Concentrations (ASC's)
and Indicated Standard Concentrations (ISC's)

| Compound Name | Reference Spectrum File Name | ASC (ppm) | ISC (ppm) Analytes i=1.....I Interferants j=1.....J | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |

FIGURE F.2

Presentation of Fractional Calibration Uncertainties (FCU's)
and Analytical Uncertainties (AU's)

| Analyte Name | FCU (%) | AU (%) |
|---|---|---|
| | | |
| | | |

## APPENDIX G

MEASURING NOISE LEVELS

### G.1 General

The root-mean-square (RMS) noise level is the standard measure of noise. The RMS noise level of a contiguous segment of a spectrum is the RMSD between the absorbance values that form the segment and the mean value of the segment (see Appendix A).

### G.2 Calculations

G.2.1 Evacuate the absorption cell or fill it with UPC grade nitrogen at approximately one atmosphere total pressure.

G.2.2 Record two single beam spectra of signal integration period $t_{SS}$.

G.2.3 Form the double beam absorption spectrum from these two single beam spectra, and calculate the noise level $RMS_{Sm}$ in the M analytical regions.

## APPENDIX H

## DETERMINING SAMPLE ABSORPTION PATHLENGTH ($L_S$) AND FRACTIONAL ANALYTICAL UNCERTAINTY (FAU)

### H.1 General

Reference spectra recorded at absorption pathlength ($L_R$), gas pressure ($P_R$), and gas absolute temperature ($T_R$) may be used to determine analyte concentrations in samples whose spectra are recorded at conditions different from that of the reference spectra, i.e., at absorption pathlength ($L_S$), absolute temperature ($T_S$), and pressure ($P_S$). Appendix H describes the calculations for estimating the fractional uncertainty (FAU) of this practice. It also describes the calculations for determining the sample absorption pathlength from comparison of CTS spectra, and for preparing spectra for further instrumental and procedural checks.

H.1.1 Before sampling, determine the sample absorption pathlength using least squares analysis. Determine the ratio $L_S/L_R$ by comparing the spectral sets {R1} and {R3}, which are recorded using the same CTS at $L_S$ and $L_R$, and $T_S$ and $T_R$, but both at $P_R$.

H.1.2 Determine the fractional analysis uncertainty (FAU) for each analyte by comparing a scaled CTS spectral set, recorded at $L_S$, $T_S$, and $P_S$, to the CTS reference spectra of the same gas, recorded at $L_R$, $T_R$, and $P_R$. Perform the quantitative comparison after recording the sample spectra, based on band areas of the spectra in the CTS absorbance band associated with each analyte.

### H.2 Calculations

H.2.1 Absorption Pathlength Determination. Perform and document separate linear baseline corrections to each analytical region in the spectral sets {R1} and {R3}. Form a one-dimensional array $\mathbf{A}_R$ containing the absorbance values from all segments of {R1} that are associated with the analytical regions; the members of the array are $A_{Ri}$, i = 1, n. Form a similar one-dimensional array $\mathbf{A}_S$ from the absorbance values in the spectral set {R3}; the members of the array are $A_{Si}$, i = 1, n. Based on the model $\mathbf{A}_S = r\mathbf{A}_R + \mathbf{E}$, determine the least-squares estimate of r', the value of r which minimizes the square error $\mathbf{E}^2$. Calculate the sample absorption pathlength $L_S = r'(T_S/T_R)L_R$.

H.2.2 Fractional Analysis Uncertainty. Perform and document separate linear baseline corrections to each analytical region in the spectral sets {R1} and {R4}. Form the arrays $\mathbf{A}_S$ and $\mathbf{A}_R$ as described in Section H.2.1, using values from {R1} to form $\mathbf{A}_R$, and values from {R4} to form $\mathbf{A}_S$. Calculate the values

$$NRMS_E = \sqrt{\sum_{i=1}^{n} \left[ A_{Si} - \left(\frac{T_R}{T_S}\right)\left(\frac{L_S}{L_R}\right)\left(\frac{P_S}{P_R}\right) A_{Ri} \right]^2} \qquad (9)$$

and

$$IA_{AV} = \frac{1}{2} \sum_{i=1}^{n} \left[ A_{Si} + \left(\frac{T_R}{T_S}\right)\left(\frac{L_S}{L_R}\right)\left(\frac{P_S}{P_R}\right) A_{Ri} \right] \qquad (10)$$

The fractional analytical uncertainty is defined as

$$FAU = \frac{NRMS_E}{IA_{AV}} \qquad (11)$$

## APPENDIX I

DETERMINING FRACTIONAL MODEL UNCERTAINTIES (FMU)

### I.1 General

To prepare analytical programs for FTIR analyses, the sample constituents must first be assumed; the calculations in this appendix, based upon a simulation of the sample spectrum, verify the appropriateness of these assumptions. The simulated spectra consist of the sum of single compound reference spectra scaled to represent their contributions to the sample absorbance spectrum; scaling factors are based on the indicated standard concentrations (ISC) and measured (sample) analyte and interferant concentrations, the sample and reference absorption pathlengths, and the sample and reference gas pressures. No band-shape correction for differences in the temperature of the sample and reference spectra gases is made; such errors are included in the FMU estimate. The actual and simulated sample spectra are quantitatively compared to determine the fractional model uncertainty; this comparison uses the reference spectra band areas and residuals in the difference spectrum formed from the actual and simulated sample spectra.

### I.2 Calculations

I.2.1 For each analyte (with scaled concentration $RSA_i$), select a reference spectrum $SA_i$ with indicated standard concentration $ISC_i$. Calculate the scaling factors

$$RA_i = \frac{T_R L_S P_S RSA_i}{T_S L_R P_R ISC_i} \qquad (12)$$

and form the spectra $SAC_i$ by scaling each $SA_i$ by the factor $RA_i$.

I.2.2 For each interferant, select a reference spectrum $SI_k$ with indicated standard concentration $ISC_k$. Calculate the scaling factors

$$RI_k = \frac{T_R L_S P_S RSI_k}{T_S L_R P_R ISC_k} \qquad (13)$$

and form the spectra $SIC_k$ by scaling each $SI_k$ by the factor $RI_k$.

I.2.3 For each analytical region, determine by visual inspection which of the spectra $SAC_i$ and $SIC_k$ exhibit absorbance bands within the analytical region. Subtract each spectrum $SAC_i$

and $SIC_k$ exhibiting absorbance from the sample spectrum $S_S$ to form the spectrum $SUB_S$. To save analysis time and to avoid the introduction of unwanted noise into the subtracted spectrum, it is recommended that the calculation be made (1) only for those spectral data points within the analytical regions, and (2) for each analytical region separately using the original spectrum $S_S$.

I.2.4 For each analytical region m, calculate the RMSD of $SUB_S$ between the absorbance values and their mean in the region $FFU_m$ to $FFL_m$. Denote the result by $RMSS_m$.

I.2.5 For each analyte i, calculate the quantity

$$FM_m = \frac{RMSS_m (FFU_m - FFL_m) AU_i DL_i}{AAI_i RSA_i} \qquad (14)$$

for each analytical region associated with the analyte.

I.2.6 If only the $m^{th}$ analytical region is used to calculate the concentration of the $i^{th}$ analyte, set $FMU_i = FM_m$.

I.2.7 If a number of analytical regions are used to calculate the concentration of the $i^{th}$ analyte, set $FM_i$ equal to the weighted mean of the appropriate $FM_m$ values calculated above. Mathematically, if the set of analytical regions employed is $\{m'\}$, then

$$FMU_i = \sum_{k \in \{m'\}} W_{ik} FM_k \qquad (15)$$

where $W_{ik}$ is calculated as described in Appendix D.

## APPENDIX J

### DETERMINING OVERALL CONCENTRATION UNCERTAINTIES (OCU)

The calculations in previous sections and appendices estimate the measurement uncertainties for various FTIR measurements. The lowest possible overall concentration uncertainty (OCU) for an analyte is its MAU value, which is an estimate of the absolute concentration uncertainty when spectral noise dominates the measurement error. However, if the product of the largest fractional concentration uncertainty (FRU, FCU, FAU, or FMU) and the measured concentration of an analyte exceeds the MAU for the analyte, then the OCU is this product. In mathematical terms, set $OFU_i = MAX\{FRU_i, FCU_i, FAU_i, FMU_i\}$ and $OCU_i = MAX\{RSA_i * OFU_i, MAU_i\}$.

## APPENDIX K

SPECTRAL DE-RESOLUTION PROCEDURES

### K.1 General.

High resolution reference spectra can be converted into lower resolution standard spectra for use in quantitative analysis of sample spectra. This is accomplished by truncating the number of data points in the original reference sample and background interferograms.

De-resolved spectra must meet the following requirements to be used in quantitative analysis.

(a) The resolution must match the instrument sampling resolution. This is verified by comparing a de-resolved CTS spectrum to a CTS spectrum measured on the sampling instrument.

(b) The Fourier transformation of truncated interferograms (and their conversion to absorbance spectra) is performed using the same apodization function (and other mathematical corrections) used in converting the sample interferograms into absorbance spectra.

### K.2 Procedures

This section details three alternative procedures using two different commercially available software packages. A similar procedures using another software packages is acceptable if it is based on truncation of the original reference interferograms and the results are verified by Section K.3.

K.2.1 KVB/Analect Software Procedure - The following example converts a 0.25 $cm^{-1}$ 100 ppm ethylene spectrum (cts0305a) to 1 $cm^{-1}$ resolution. The 0.25 $cm^{-1}$ CTS spectrum was collected during the EPA reference spectrum program on March 5, 1992. The original data (in this example) are in KVB/Analect FX-70 format.

(i) **decomp cts0305a.aif,0305dres,1,16384,1**

"decomp" converts cts0305a to an ASCII file with name 0305dres. The resulting ASCII interferogram file is truncated to 16384 data points. Convert background interferogram (bkg0305a.aif) to ASCII in the same way.

(ii) **compose 0305dres,0305dres.aif,1**

"Compose" transforms truncated interferograms back to spectral format.

(iii) **IG2SP 0305dres.aif,0305dres.dsf,3,1,low $cm^{-1}$,high $cm^{-1}$**

"IG2SP" converts interferogram to a single beam spectrum using Norton-Beer medium apodization, 3, and no zero filling, 1. De-resolved interferograms should be transformed using the same apodization and zero filling that will be used to collect sample spectra. Choose the desired low and high frequencies, in $cm^{-1}$. Transform the background interferogram in the same way.

(iv) **DVDR 0305dres.dsf,bkg0305a.dsf,0305dres.dlf**

"DVDR" ratios the transformed sample spectrum against the background.

(v) **ABSB 0305dres.dlf,0305dres.dlf**

"ABSB" converts the spectrum to absorbance.

The resolution of the resulting spectrum should be verified by comparison to a CTS spectrum collected at the nominal resolution. Refer to Section K.3.

K.2.2 Alternate KVB/Analect Procedure -- In either DOS (FX-70) or Windows version (FX-80) use the "Extract" command directly on the interferogram.

(i) **EXTRACT CTS0305a.aif,0305dres.aif,1,16384**

"Extract" truncates the interferogram to data points from to 16384 (or number of data points for desired nominal resolution). Truncate background interferogram in the same way.

(ii) Complete steps (iii) to (v) in Section K.2.1.

K.2.3 Grams™ Software Procedure - Grams™ is a software package that displays and manipulates spectra from a variety of instrument manufacturers. This procedure assumes familiarity with basic functions of Grams™.

This procedure is specifically for using Grams to truncate and transform reference interferograms that have been imported into Grams from the KVB/Analect format. Table K-1 shows data files and parameter values that are used in the following procedure.

The choice of all parameters in the ICOMPUTE.AB call of step 3 below should be fixed to the shown values, with the exception of the "Apodization" parameter. This parameter should be set (for both background and sample single beam conversions) to the type of apodization function chosen for the de-resolved spectral library.

TABLE K-1. GRAMS DATA FILES AND DE-RESOLUTION PARAMETERS.

| Desired Nominal Spectral Resolution ($cm^{-1}$) | Data File Name | Parameter "N" Value |
|---|---|---|
| 0.25 | Z00250.sav | 65537 |
| 0.50 | Z00500.sav | 32769 |
| 1.0 | Z01000.sav | 16385 |
| 2.0 | Z02000.sav | 8193 |

(i) **Import** using "File/Import" the desired *.aif file. Clear all open data slots.

(ii) **Open** the resulting *.spc interferogram as file #1.

(iii) **Xflip** - *If the x-axis is increasing from left to right, and the ZPD burst appears near the left end of the trace, omit this step.*

In the "Arithmetic/Calc" menu item input box, type the text below. Perform the calculation by clicking on "OK" (once only), and, when the calculation is complete, click the "Continue" button to proceed to step (iv). Note the comment in step (iii) regarding the trace orientation.

**xflip:#s=#s(#0,#N)+50**

(iv) **Run ICOMPUTE.AB** from "Arithmetic/Do Program" menu. Ignore the "subscripting error," if it occurs.

The following menu choices should be made before execution of the program (refer to Table K-1 for the correct choice of "N":)

First: **N** Last: **0** Type: **Single Beam**
Zero Fill: **None** Apodization: **(as desired)**
Phasing: **User**
Points: **1024** Interpolation: **Linear** Phase:
**Calculate**

(v) **As** in step (iii), in the "**Arithmetic/Calc**" menu item enter and then run the following commands (refer to Table 1 for appropriate "**FILE,**" which may be in a directory other than "c:\mdgrams.")

**setffp 7898.8805, 0 : loadspc "c:\mdgrams\ FILE" : #2=#s+#2**

(vi) Use "**Page Up**" to activate file #2, and then use the "**File/Save As**" menu item with an appropriate file name to save the result.

## K.3 Verification of New Resolution

K.3.1 Obtain interferograms of reference sample and background spectra. Truncate interferograms and convert to absorbance spectra of desired nominal resolution.

K.3.2 Document the apodization function, the level of zero filling, the number of data points, and the nominal resolution of the resulting de-resolved absorbance spectra. Use the identical apodization and level of zero filling when collecting sample spectra.

K.3.3 Perform the same de-resolution procedure on CTS interferograms that correspond with the reference spectra (reference CTS) to obtain de-resolved CTS standard spectra (CTS standards). Collect CTS spectra using the sampling resolution and the FTIR system to be used for the field measurements (test CTS). If practical, use the same pathlength, temperature, and standard concentration that were used for the reference CTS. Verify, by the following procedure that CTS linewidths and intensities are the same for the CTS standards and the test CTS.

K.3.4 After applying necessary temperature and pathlength corrections (document these corrections), subtract the CTS standard from the test CTS spectrum. Measure the RMSD in the resulting subtracted spectrum in the analytical region(s) of the CTS band(s). Use the following equation to compare this RMSD to the test CTS band area. The ratio in equation 7 must be no greater than 5 percent (0.05).

$$\frac{RMSS_i \times n(FFU_i - FFL_i)}{A_{CTS\text{-}test}} \leq .05 \qquad (16)$$

RMSS=RMSD in the $i^{th}$ analytical region in subtracted result, test CTS minus CTS standard.

n=number of data points per $cm^{-1}$. Exclude zero filled points.

$FFU_i$ &=The upper and lower limits ($cm^{-1}$), respectively, of the $FFL_i$ analytical region.

$A_{test\text{-}CTS}$=band area in the $i^{th}$ analytical region of the test CTS.

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| EPA-454/R-99-051 | | |

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

The purpose of this project was to measure organic and inorganic hazardous air pollutants (HAPs) using a test method based on Fourier Transform Infrared Spectroscopy. This report describes the test procedures and presents results of the testing at Eastern Ridge Lime plant in Ripplemead, Virginia.

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