



## Project Summary

# Testing the Performance of Real-Time Incinerator Emission Monitors

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In a recently completed test program at the U.S. Environmental Protection Agency (EPA) Incineration Research Facility (IRF), ten prototype or developing continuous emission monitors (CEMs) for measuring trace metal or trace organic species concentrations were tested. Of the ten CEMs tested, four measured concentrations of several specific volatile organic compounds (VOCs), one measured total particulate-bound polynuclear aromatic hydrocarbon concentrations, two measured concentrations of up to 14 trace metals, and three measured mercury concentrations. While the testing consisted of obtaining quantitative measurement data on the four measures of CEM performance checked in a relative accuracy test audit as described in 40 CFR 60 Appendix F—relative accuracy (RA), calibration drift (CD), zero drift (ZD), and response time—the primary project objective focused on the RA measurement. The RA measurement was achieved by comparing the monitored analyte concentration reported by the CEM to the concentration determined by the EPA reference method (RM) for the analyte. Four series of tests were performed, each simultaneously testing up to three monitors measuring the same or similar analyte type. Each test series consisted of performing triplicate RM measurements at each of three target flue gas monitored analyte concentrations while the tested CEMs were in operation. All measurements were taken in the wet scrubber exit flue gas

from the pilot-scale rotary kiln incineration system at the IRF.

The test program results clearly showed the prototype nature of most approaches tested, and the clear need for further development. Mercury CEMs will require the least development and are nearly commercial offerings. However, the approaches tested for multi-metals and VOC determinations require further development. Given this need, the importance of continuing test programs of the scope and scale of this one cannot be overemphasized.

*This Project Summary was developed by EPA's National Risk Management Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

EPA is currently developing more stringent emission standards and considering changes in the way that permits for waste combustion facilities are handled. More public involvement in the process has been proposed. Because the public's apparent perception of incinerators is that high concentrations of hazardous compounds are continually being released from the stacks of the thermal treatment devices, a means by which the "real-time" (defined as ranging from instantaneous to within several hours) organic and metals emissions can be monitored would be of great benefit to both regulators and the regulated commu-

nity. The ability to have “immediate” knowledge of stack emissions would provide assurances that the thermal treatment device is operating correctly or indicate the change of operating conditions needed to adjust stack emissions. Thus, having this monitoring capability would constitute one means of responding to and allaying the public’s fears by showing that good, safe, and clean combustion practices can be demonstrated.

Several developers have designed monitoring units that they claim will measure various regulated hazardous compounds using a number of different innovative concepts and technologies. The development of these CEM approaches for both trace metal and trace organic analyte classes has advanced to the state that several candidate approaches are now in the prototype instrument stage. Given this, the general objective of the project reported herein was to test several prototype instruments and establish or estimate for each unit the effectiveness, reliability, accuracy, and detection limit.

For this test program, ten developing CEM approaches were tested. These are listed in Table 1 by monitored analyte class. As shown, included in the list of CEMs tested in this program are one semivolatile organic constituent (SVOC), four VOC, two multi-metal, and three mercury CEMs.

## Test Program

The selected approaches evaluated in this test program were performed in the pilot-scale rotary kiln incineration system (RKS) at EPA’s IRF, located in Jefferson, AR. The testing consisted of obtaining quantitative measurement data on four measures of CEM performance checked in a relative accuracy test audit of a CEM as described in 40 CFR 60 Appendix F. These measures are RA, CD, ZD, and response time.

Measuring a CEM’s RA requires comparing the monitored analyte concentration reported by the CEM to the concentration determined by the RM for the analyte. In this program, the RM for trace metal (including mercury) monitors was draft Method 29, the EPA multiple metals method documented in the boiler and industrial furnace rules. The RM for VOCs was Method 0030 with analysis using thermal desorption, purge and trap by Method 5040, and quantitation by Method 8015A. The RM for SVOCs was Method 0010 with analysis by Method 8270B.

## Test Facility

Figure 1 is a process schematic of the RKS as configured for these tests. The RKS consists of a primary combustion chamber, a transition section, and a fired afterburner chamber. After exiting the afterburner extension, flue gas flows through a quench section that is followed by a

primary air pollution control system (APCS). The initial element of the primary APCS for these tests was the venturi scrubber/packed-column scrubber combination shown in Figure 1. This scrubber system removes from the flue gas most of the coarse particles and any acid gas, such as HCl. Following the scrubber system, the flue gas is reheated to about 120°C (250°F) by a 100-kW electric duct heater, then passed through a fabric filter (baghouse). The baghouse removes most of the remaining flue gas particles. Downstream of the baghouse, a backup, secondary APCS, comprised of an activated-carbon adsorber and a high-efficiency particulate air filter is in place. The CEMs tested in this program sampled flue gas at the scrubber exit location.

## Testing Procedures

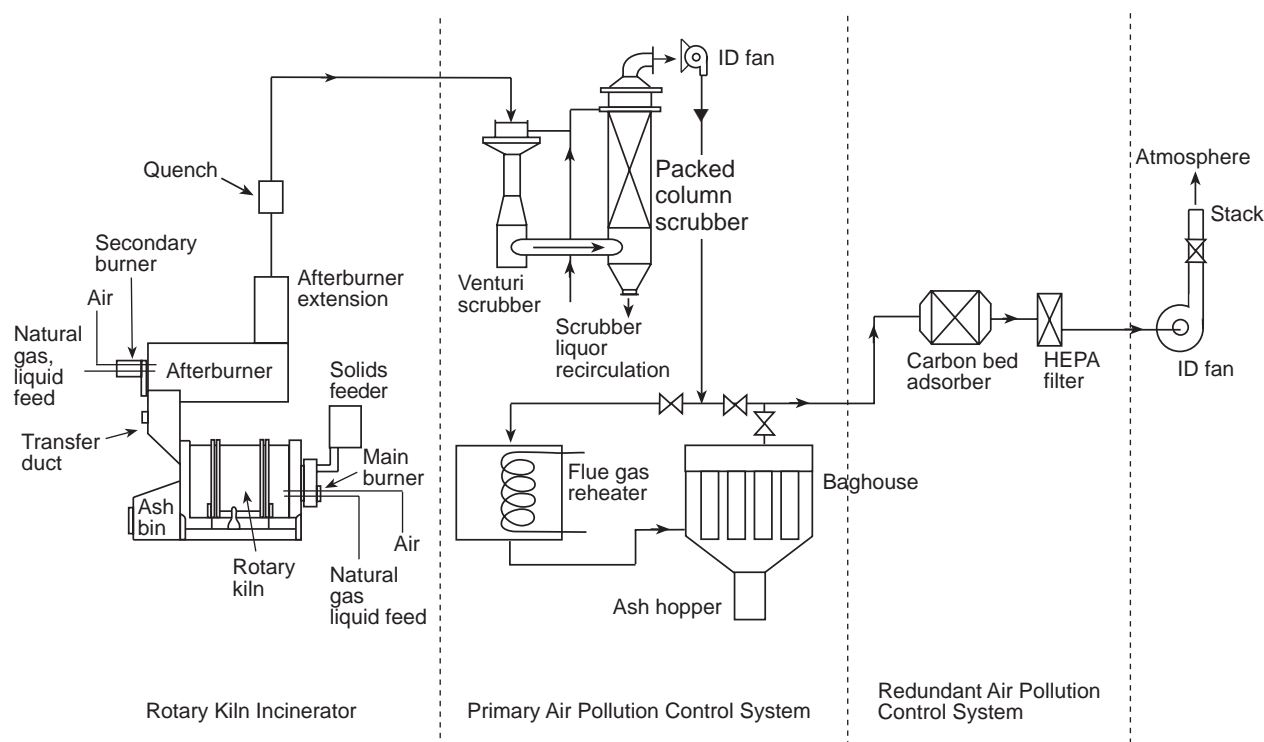
The test program consisted of four series of tests; each series tested one set of CEMs, generally monitoring the same analyte set. Up to three CEMs were tested at the same time during each of the four test series. The major portion of the test program consisted of performing three sequential RM measurements, while the tested CEMs were in operation, at each of three flue gas concentrations of monitored analytes. Thus, each test series was designed to supply nine sets of parallel RM and CEM reading data, three at each of three analyte concentrations. These nine sets of parallel RM and CEM data supported the calculation of each CEM’s RA. Thus, up to three RAs were calculated for each CEM, one at each of the three flue gas concentrations tested. Other test efforts supported the measurements of CD, ZD, and response time.

## Test Waste Feed

The incinerator feed material was a synthetic hazardous waste comprised of an attapulgite clay solid sorbent combined with a mixture of 14 trace metals and VOCs. The mixture of VOCs added to the sorbent base contained 76% toluene by weight, with 12% each of chlorobenzene and tetrachloroethene. This mixture was combined with the clay sorbent in the ratio of 1.0 kg of organic constituent mixture to 2.4 kg of clay. The mixture was a free-flowing solid with no freestanding liquid and was continuously fed to the RKS via a screw feeder system. For all tests, the target clay/organic mixture feedrate was 68 kg/hr (150 lb/hr). The target kiln exit gas temperature was 870°C (1,600°F), and the target afterburner exit gas temperature was 1,065°C (1,950°F).

**Table 1.** Participants in the CEM Test Program

| Monitored Analyte | Developer  | Approach  |
|-------------------|--|---|
| SVOCs             | EcoChem  | Photoionization of aerosol-bound polycyclic aromatic hydrocarbons                     |
| VOCs              | EcoLogic   | Continuous chemical ionization mass spectrometry                                      |
|                   | Marine Shale Processors (MSP)                              | Continuous online mass spectrometry   |
|                   | Oak Ridge National Laboratory (ORNL)                       | Direct sampling ion trap mass spectrometry  |
|                   | EPA, Air Pollution Prevention and Control Division (APPCD) | Online gas chromatography with dual flame ionization, electron capture detection      |
| Multi-metals      | Sandia National Laboratories (SNL)                         | Laser induced plasma spectroscopy   |
|                   | Metorex  | Extractive beta gauge particulate monitor with x-ray fluorescence metals analysis     |
| Mercury           | Perkin-Elmer   | Gold trap amalgamation collection, cold vapor atomic absorption spectroscopy analysis |
|                   | Senova   | Noble metal film solid state chemical microsensor                                     |
|                   | EcoChem  | Cold vapor atomic absorption spectroscopy   |



**Figure 1.** Schematic of the IRF rotary kiln incineration system.

## Multi-Metal and Mercury CEM Tests

The trace metals of interest to the test program are listed in Table 2, which also notes the program target scrubber exit flue gas concentrations of each metal for the tests of multi-metals CEMs. For the mercury CEMs tests in Test Series 3, the low concentration targets were at half the levels noted in the low concentration column in Table 2. The intermediate concentration targets were those noted in the low concentration column in Table 2. The high concentration targets were those noted in the intermediate concentration column in Table 2. This change was incorporated at the request of the mercury CEM developers.

Trace metals were added to the RKS, to result in scrubber exit flue gas levels, via two routes. Both routes used an aqueous spike solution of the metals. A concentrated solution was added for the multi-metal CEM test days at the high target flue gas metals concentration. This concentrated solution was diluted for the multi-metal CEM test days at the intermediate and low target concentrations and

for the mercury CEM tests. The two routes of metals addition were incorporated into the clay/organic mixture and atomized into the kiln main burner flame.

## VOC and SVOC CEM Tests

The VOCs present in the scrubber exit flue gas for all tests included benzene, carbon tetrachloride, chlorobenzene, chloroform, 1,2-dichloroethane, 1,1-dichloroethene, tetrachloroethene, toluene, 1,1,1-trichloroethane, and trichloroethene. The target flue gas concentrations of the compounds were in the 2, 20, and 200  $\mu\text{g/dscm}$  ranges (low, intermediate, and high concentrations). Naphthalene, phenanthrene, and pyrene were the SVOCs introduced into the flue gas for all tests, at the same target flue gas concentrations noted above.

The VOCs and SVOCs were introduced into the flue gas by metering a solution of the spiking compounds in methanol through a length of fine bore stainless steel tubing into the afterburner extension at its centerline. The afterburner exit flue gas was partially quenched to a temperature of between 360° to 427°C (680° and 800°F) by a water spray introduced at the

**Table 2.** Test Trace Metals and Target Flue Gas Concentrations

| Metal          | Target Flue Gas Concentration, $\mu\text{g/dscm}$ |              |       |
|----------------|---|--------------|-------|
|                | Low   | Intermediate | High  |
| Antimony (Sb)  | 10  | 40           | 400   |
| Arsenic (As)   | 5   | 20           | 200   |
| Barium (Ba)    | 50  | 200          | 2,000 |
| Beryllium (Be) | 0.5   | 2            | 20    |
| Cadmium (Cd)   | 5   | 20           | 200   |
| Chromium (Cr)  | 20  | 80           | 560   |
| Cobalt (Co)    | 10  | 40           | 400   |
| Lead (Pb)      | 50  | 200          | 2,000 |
| Manganese (Mn) | 5   | 20           | 200   |
| Mercury (Hg)   | 20  | 80           | 800   |
| Nickel (Ni)    | 10  | 40           | 400   |
| Selenium (Se)  | 40  | 200          | 2,000 |
| Silver (Ag)    | 5   | 20           | 200   |
| Thallium (Tl)  | 5   | 20           | 200   |

beginning of the afterburner extension. A concentrated organic spiking solution was prepared and used for the high target flue gas VOC and SVOC CEM tests. The concentrated solution was diluted appropriately for the intermediate and low target flue gas concentration tests.

## Test Results

### VOC CEM Tests

Tables 3 through 5 present the results of the three sequential RM measurements, along with the Oak Ridge National Labo-

ratory (ORNL) and EcoLogic CEM results, for each of the three VOC concentrations tested in Test Series 1. The EcoLogic CEM data for the first day of testing at the low VOC concentration were not reported in EcoLogic's test report because of operator error that resulted in CEM readings that were inflated and incorrect. RAs calculated using the RM and CEM data in Tables 3 through 5 are summarized in Table 6. The data in Table 6 show that the calculated RAs for the ORNL CEM ranged from 123% to 305% at the low test

concentration, with an average of 196% over the seven compounds reported. ORNL CEM RAs were improved at the intermediate test concentration, at 113% to 278%, with an average of 154% over the nine compounds reported. Further improvement is seen at the high test concentration, with an RA range of 84% to 144%, and an average of 105% over all ten compounds reported. In fact, the RA for all VOCs reported uniformly improved as the test concentration increased.

**Table 3.** Measured Flue Gas Concentrations for the Test of the ORNL and EcoLogic CEMs at the Low VOC Concentration

| Compound              | Concentration, µg/dscm |      |                 |              |      |           |              |      |           |
|-----------------------|------------------------|------|-----------------|--------------|------|-----------|--------------|------|-----------|
|                       | 1st Daily RM           |      |                 | 2nd Daily RM |      |           | 3rd Daily RM |      |           |
|                       | RM                     | ORNL | Eco-Logic       | RM           | ORNL | Eco-Logic | RM           | ORNL | Eco-Logic |
| Benzene               | 32.4                   | 1.3  | NO <sup>a</sup> | 41.9         | 1.6  | NO        | 59.6         | 1.6  | NO        |
| Carbon tetrachloride  | 31.2                   | <0.4 | NO              | 34.2         | <0.4 | NO        | 38.0         | 0.92 | NO        |
| Chlorobenzene         | 55.6                   | 0.76 | NO              | 49.2         | 1.2  | NO        | 86.7         | 5.6  | NO        |
| Chloroform            | 40.8                   | 0.56 | NO              | 47.3         | 0.4  | NO        | 41.6         | 3.6  | NO        |
| 1,2-Dichloroethane    | 2.4                    | 2.5  | NO              | 3.3          | 1.5  | NO        | 2.6          | 6.8  | NO        |
| 1,1-Dichloroethene    | 86.4                   | 3.2  | NO              | 35.6         | <0.4 | NO        | 16.9         | 11.0 | NO        |
| Tetrachloroethene     | 89.9                   | 1.7  | NO              | 73.9         | 1.3  | NO        | 126          | 4.3  | NO        |
| Toluene               | 352                    | 9.2  | NO              | 316          | 9.2  | NO        | 462          | 16   | NO        |
| 1,1,1-Trichloroethane | 2.5                    | <0.4 | NO              | 4.6          | <0.4 | NO        | 6.4          | <0.4 | NO        |
| Trichloroethene       | 6.9                    | <0.4 | NO              | 5.9          | <0.4 | NO        | 3.9          | <0.4 | NO        |

<sup>a</sup>NO=CEM not operational.

**Table 4.** Measured Flue Gas Concentrations for the Test of the ORNL and EcoLogic CEMs at the Intermediate VOC Concentration

| Compound              | Concentration, µg/dscm |      |           |              |      |           |              |      |           |
|-----------------------|------------------------|------|-----------|--------------|------|-----------|--------------|------|-----------|
|                       | 1st Daily RM           |      |           | 2nd Daily RM |      |           | 3rd Daily RM |      |           |
|                       | RM                     | ORNL | Eco-Logic | RM           | ORNL | Eco-Logic | RM           | ORNL | Eco-Logic |
| Benzene               | 32.7                   | 12.0 | 97        | 28.7         | <2.3 | 820       | 36.4         | 5.5  | 870       |
| Carbon tetrachloride  | 46.9                   | 10.1 | 7.9       | 41.7         | 3.8  | 24        | 58.5         | 6.4  | 16        |
| Chlorobenzene         | 59.8                   | 25.8 | 81        | 46.3         | 7.2  | 81        | 74.3         | 27.6 | 98        |
| Chloroform            | 57.1                   | 23.9 | 140       | 56.7         | 9.6  | 230       | 66.3         | 18.4 | 170       |
| 1,2-Dichloroethane    | 17.4                   | 43.3 | 210       | 12.3         | 16.6 | 340       | 15.3         | 29.5 | 290       |
| 1,1-Dichloroethene    | 24.0                   | 55.3 | 320       | 20.5         | 26.7 | 430       | 14.3         | 40.5 | 370       |
| Tetrachloroethene     | 81.4                   | 11.1 | 120       | 64.1         | 2.5  | 770       | 101          | 7.4  | 710       |
| Toluene               | 342                    | 147  | 210       | 218          | 71.8 | 120       | 413          | 103  | 250       |
| 1,1,1-Trichloroethane | 13.8                   | <2.3 | 800       | 13.3         | <2.3 | 910       | 12.9         | <2.3 | 840       |
| Trichloroethene       | 19.4                   | 4.6  | 420       | 18.6         | 0.9  | 770       | 20.4         | 1.8  | 510       |

**Table 5.** Measured Flue Gas Concentrations for the Test of the ORNL and EcoLogic CEMs at the High VOC Concentration

| Compound              | Concentration, µg/dscm |      |           |              |      |           |              |      |           |
|-----------------------|------------------------|------|-----------|--------------|------|-----------|--------------|------|-----------|
|                       | 1st Daily RM           |      |           | 2nd Daily RM |      |           | 3rd Daily RM |      |           |
|                       | RM                     | ORNL | Eco-Logic | RM           | ORNL | Eco-Logic | RM           | ORNL | Eco-Logic |
| Benzene               | 102                    | 36.8 | 140       | 89.1         | 50.7 | 160       | 91.3         | 28.6 | 190       |
| Carbon tetrachloride  | 423                    | 101  | 380       | 409          | 119  | 350       | 446          | 76.4 | 360       |
| Chlorobenzene         | 337                    | 138  | 250       | 299          | 170  | 270       | 269          | 97.6 | 280       |
| Chloroform            | 417                    | 101  | 330       | 411          | 168  | 350       | 413          | 91.2 | 390       |
| 1,2-Dichloroethane    | 184                    | 88.4 | 450       | 174          | 114  | 500       | 183          | 6.3  | 540       |
| 1,1-Dichloroethene    | 116                    | 38.7 | 350       | 140          | 44.2 | 440       | 162          | 35.9 | 480       |
| Tetrachloroethene     | 429                    | 62.6 | 690       | 374          | 61.7 | 740       | 324          | 37.8 | 690       |
| Toluene               | 1,760                  | 847  | 1,300     | 1,393        | 921  | 1,200     | 1,024        | 460  | 760       |
| 1,1,1-Trichloroethane | 175                    | 24.9 | 170       | 164          | 37.8 | 190       | 182          | 20.3 | 210       |
| Trichloroethene       | 189                    | 15.7 | 340       | 176          | 19.3 | 300       | 185          | 14.7 | 360       |

**Table 6.** Relative Accuracies of the ORNL and EcoLogic CEMs

| Compound              | RA, %              |              |          |                    |              |         |
|-----------------------|--------------------|--------------|----------|--------------------|--------------|---------|
|                       | ORNL               |              |          | EcoLogic           |              |         |
|                       | Test Concentration |              |          | Test Concentration |              |         |
|                       | Low                | Intermediate | High     | Low                | Intermediate | High    |
| Benzene               | 173                | 119          | 98       | NC                 | 5,020        | 154     |
| Carbon tetrachloride  | NC <sup>a</sup>    | 129          | 100      | NC                 | 135          | 27      |
| Chlorobenzene         | 164                | 93           | 84       | NC                 | 74           | 52      |
| Chloroform            | 123                | 105          | 97       | NC                 | 396          | 33      |
| 1,2-Dichloroethane    | 305                | 278          | 144      | NC                 | 2,890        | 239     |
| 1,1-Dichloroethene    | 299                | 277          | 115      | NC                 | 2,520        | 283     |
| Tetrachloroethene     | 162                | 142          | 113      | NC                 | 1,640        | 128     |
| Toluene               | 145                | 131          | 88       | NC                 | 65           | 47      |
| 1,1,1-Trichloroethane | NC                 | NC           | 110      | NC                 | 7,320        | 36      |
| Trichloroethene       | NC                 | 113          | 103      | NC                 | 5,140        | 116     |
| Average <sup>b</sup>  | 196                | 154          | 105      | NC                 | 2,520        | 121     |
| Median <sup>b</sup>   | 164                | 129          | 100, 103 | NC                 | 1,640, 2,520 | 52, 116 |

<sup>a</sup> NC=Not calculated.<sup>b</sup> Average and median excludes NC entries.

For the intermediate test concentration, the RAs of the EcoLogic CEM ranged from 65% to 7,320%, with an average of 2,520%. Improved performance was seen at the high test concentration, for which the RA ranged from 27% to 283% and averaged 121%. As seen for the ORNL CEM, the RAs for nine of the ten VOCs reported were improved at the high test concentration compared to the intermediate concentration.

Tables 7 through 9 present the results of the three sequential RM measurements, along with the EPA/APPCD and MSP CEM results, for each of the three VOC concentrations tested in Test Series 4. The tables indicate that, out of the nine sampling periods, MSP obtained data for only two periods. RAs corresponding to the RM/CEM concentration data given in Tables 7 through 9 are summarized in Table 10. The data in Table 10 show that the RAs for the EPA CEM ranged from 71% to 3,190% and averaged 638% for the low test concentrations. The relatively high average RA was driven by the two very high RAs for 1,2-dichloroethane and 1,1-dichloroethene. These two compounds were found in EPA/APPCD system blanks. EPA/APPCD's decision not to blank-correct their data led to the corresponding high RAs. The median RA for the low concentration test at a much improved 113%

**Table 7.** Measured Flue Gas Concentrations for the Test of the EPA/APPCD and MSP CEMs at the Low VOC Concentration

| Compound              | Concentration, µg/dscm |               |                 |              |               |       |              |               |       |
|-----------------------|------------------------|---------------|-----------------|--------------|---------------|-------|--------------|---------------|-------|
|                       | 1st Daily RM           |               |                 | 2nd Daily RM |               |       | 3rd Daily RM |               |       |
|                       | RM                     | EPA/<br>APPCD | MSP             | RM           | EPA/<br>APPCD | MSP   | RM           | EPA/<br>APPCD | MSP   |
| Benzene               | 8.2                    | 21.31         | NO <sup>a</sup> | 5.9          | 29.93         | 795   | 8.4          | 22.21         | 707   |
| Carbon tetrachloride  | 13.9                   | 9.68          | NO              | 11.9         | 5.99          | 118   | 13.3         | 4.99          | 126   |
| Chlorobenzene         | 21.6                   | 18.56         | NO              | 20.8         | 29.16         | 143   | 16.0         | 18.8          | 60.2  |
| Chloroform            | 15.8                   | 16.95         | NO              | 18.4         | 14.89         | 3,439 | 15.8         | 9.25          | 1,515 |
| 1,2-Dichloroethane    | 1.8                    | 43.21         | NO              | 1.5          | 39.18         | 73.7  | 1.6          | 30.33         | 78.5  |
| 1,1-Dichloroethene    | 2.0                    | 76.34         | NO              | 6.3          | 90.23         | 322   | 5.1          | 84.49         | 271   |
| Tetrachloroethene     | 32.7                   | 15.65         | NO              | 26.9         | 31.7          | 124   | 20.6         | 8.56          | 107   |
| Toluene               | 160.9                  | 131.92        | NO              | 149.4        | 221.38        | 1,308 | 97.1         | 57.85         | 814   |
| 1,1,1-Trichloroethane | 2.1                    | 2.21          | NO              | 1.9          | 2.22          | 3.6   | 1.8          | 3.53          | 4.1   |
| Trichloroethene       | 2.6                    | 2.18          | NO              | 2.9          | 2.71          | 3,022 | 3.0          | 1.74          | 1,602 |

<sup>a</sup>NO=Not operational.**Table 8.** Measured Flue Gas Concentrations for the Test of the EPA/APPCD and MSP CEMs at the Intermediate VOC Concentration

| Compound              | Concentration, µg/dscm |               |                 |              |               |     |              |               |     |
|-----------------------|------------------------|---------------|-----------------|--------------|---------------|-----|--------------|---------------|-----|
|                       | 1st Daily RM           |               |                 | 2nd Daily RM |               |     | 3rd Daily RM |               |     |
|                       | RM                     | EPA/<br>APPCD | MSP             | RM           | EPA/<br>APPCD | MSP | RM           | EPA/<br>APPCD | MSP |
| Benzene               | 33.9                   | 35.8          | NO <sup>a</sup> | 32.9         | 42.41         | NO  | 33.6         | 50.34         | NO  |
| Carbon tetrachloride  | 53.5                   | 31.45         | NO              | 57.8         | 37.58         | NO  | 64.1         | 40.55         | NO  |
| Chlorobenzene         | 29.5                   | 24.86         | NO              | 64.6         | 54.15         | NO  | 75.0         | 40.73         | NO  |
| Chloroform            | 43.2                   | 26.33         | NO              | 62.1         | 31.61         | NO  | 63.5         | 43.31         | NO  |
| 1,2-Dichloroethane    | 20.7                   | 27.97         | NO              | 18.1         | 34.9          | NO  | 16.6         | 55.71         | NO  |
| 1,1-Dichloroethene    | 14.2                   | 47.14         | NO              | 11.3         | 54.48         | NO  | 9.9          | 101.19        | NO  |
| Tetrachloroethene     | 39.3                   | 22.87         | NO              | 92.7         | 58.32         | NO  | 96.8         | 30.3          | NO  |
| Toluene               | 143                    | 90.22         | NO              | 498.5        | 306.1         | NO  | 551.8        | 163.48        | NO  |
| 1,1,1-Trichloroethane | 17.3                   | 13.68         | NO              | 16.2         | 14.33         | NO  | 17.4         | 14.54         | NO  |
| Trichloroethene       | 22.9                   | 16.04         | NO              | 20.6         | 16.63         | NO  | 19.1         | 15.74         | NO  |

<sup>a</sup>NO=Not operational.

to 137%, removes the dominant influence of the two compounds for which the CEM did poorly. The RAs for the EPA CEM were improved at the intermediate test concentration, ranging from 29% to 1,130% and averaging 213%. Poor performance in quantitating 1,2-dichloroethane and 1,1-

dichloroethene again accounts largely for the high average RA. Again, the median RA at 83% to 98% better reflects the mean performance of the CEM by removing the dominant influence of the RAs for the two VOCs poorly quantitated. Further improved performance of the EPA CEM

was seen at the high test concentration, with an RA range from 34% to 133% and an average RA of 73%. In fact, at the high test concentration, the RAs for two compounds poorly quantitated at the low and intermediate test concentrations are more in line with those calculated for the other



**Table 9.** Measured Flue Gas Concentrations for the Test of the EPA/APPCD and MSP CEMs at the High VOC Concentration

| Compound              | Concentration, µg/dscm |               |                 |              |               |     |              |               |     |
|-----------------------|------------------------|---------------|-----------------|--------------|---------------|-----|--------------|---------------|-----|
|                       | 1st Daily RM           |               |                 | 2nd Daily RM |               |     | 3rd Daily RM |               |     |
|                       | RM                     | EPA/<br>APPCD | MSP             | RM           | EPA/<br>APPCD | MSP | RM           | EPA/<br>APPCD | MSP |
| Benzene               | 102.6                  | 96.33         | NO <sup>a</sup> | 129.5        | 98.73         | NO  | 117.7        | 88.66         | NO  |
| Carbon tetrachloride  | 222.5                  | 209.55        | NO              | 266.2        | 205.53        | NO  | 283.7        | 135.72        | NO  |
| Chlorobenzene         | 104.8                  | 119.78        | NO              | 146.5        | 113.78        | NO  | 127.2        | 126.99        | NO  |
| Chloroform            | 229.4                  | 190.9         | NO              | 243.8        | 199.06        | NO  | 241.1        | 178.42        | NO  |
| 1,2-Dichloroethane    | 93.7                   | 95.44         | NO              | 121.2        | 107.96        | NO  | 114.9        | 90.81         | NO  |
| 1,1-Dichloroethene    | 65.9                   | 113.67        | NO              | 65.5         | 124.81        | NO  | 71.9         | 144.06        | NO  |
| Tetrachloroethene     | 112.8                  | 150.65        | NO              | 162.6        | 161.66        | NO  | 132.2        | 131.62        | NO  |
| Toluene               | 176.6                  | 191.23        | NO              | 445.4        | 213.8         | NO  | 261.5        | 217.23        | NO  |
| 1,1,1-Trichloroethane | 97.8                   | 92.89         | NO              | 106.8        | 87.31         | NO  | 103.5        | 57.93         | NO  |
| Trichloroethene       | 98.2                   | 98.46         | NO              | 114.3        | 91.81         | NO  | 113.1        | 70.04         | NO  |

<sup>a</sup>NO=Not operational.**Table 10.** Relative Accuracies of the EPA/APPCD and MSP CEMs

| Compound              | RA,%               |              |        |                    |  |  |
|-----------------------|--------------------|--------------|--------|--------------------|--|--|
|                       | EPA/APPCD          |              |        | MSP                |  |  |
|                       | Test Concentration |              |        | Test Concentration |  |  |
|                       | Low                | Intermediate | High   | Low                |  |  |
| Benzene               | 429                | 83           | 48     | 18,300             |  |  |
| Carbon tetrachloride  | 86                 | 45           | 95     | 1,200              |  |  |
| Chlorobenzene         | 87                 | 98           | 53     | 3,150              |  |  |
| Chloroform            | 76                 | 71           | 34     | 85,800             |  |  |
| 1,2-Dichloroethane    | 3,190              | 334          | 40     | 6,740              |  |  |
| 1,1-Dichloroethene    | 2,040              | 1,130        | 133    | 10,700             |  |  |
| Tetrachloroethene     | 137                | 134          | 50     | 673                |  |  |
| Toluene               | 113                | 158          | 138    | 3,040              |  |  |
| 1,1,1-Trichloroethane | 150                | 29           | 73     | 315                |  |  |
| Trichloroethene       | 71                 | 45           | 70     | 384,000            |  |  |
| Average               | 638                | 213          | 73     | 51,400             |  |  |
| Median                | 113, 137           | 83, 98       | 53, 70 | 3,150, 6,740       |  |  |

eight compounds. For this reason, the median RA at 53% to 70% is comparable to the average RA.

The calculated RAs based on the two available CEM/RM measurement pairs for the MSP CEM were quite large, ranging from 315% to 412,000% and averaging 54,600%. Even the median RAs for the MSP CEM, at 2,840% to 6,480%, are quite high.

### SVOC CEM Tests

The SVOC CEM tests were performed at the same time as the second set of VOC CEM tests. Table 11 presents the results of the three sequential RM measurements performed each test day, and compares these to the EcoChem CEM results for the test days at the low and intermediate SVOC concentrations. Due to problems in the flue gas conditioning (moisture removal) system, the EcoChem CEM could not be brought into operation on the last day of testing at the high SVOC concentration. In addition, no CEM data were obtained during the first RM period on the intermediate concentration test day because the EcoChem CEM was not in operation, again due to problems with the flue gas moisture removal system.

Table 11 also notes the RA of the EcoChem PAH CEM for the two test days the CEM was in operation. The table indicates that the RAs for the

**Table 11.** Measured Flue Gas Concentrations for the Tests of the EcoChem PAH CEMs

| Test                            | Concentration, µg/dscm |                 |              | RA,% |
|---------------------------------|------------------------|-----------------|--------------|------|
|                                 | 1st Daily RM           | 2nd Daily RM    | 3rd Daily RM |      |
| Low Concentration Test          |                        |                 |              |      |
| Naphthalene                     | 1.7                    | 1.8             | 1.7          |      |
| Phenanthrene                    | 1.3                    | 1.2             | 1.3          |      |
| Pyrene                          | 1.0                    | 0.8             | 0.9          |      |
| Total PAH                       | 4.0                    | 3.8             | 3.9          |      |
| EcoChem CEM                     | 6.9                    | 14.8            | 15.5         |      |
| Intermediate Concentration Test |                        |                 |              |      |
| Naphthalene                     | 17.5                   | 10.9            | 15.8         |      |
| Phenanthrene                    | 15.7                   | 10.1            | 15.3         |      |
| Pyrene                          | 9.1                    | 19.6            | 9.7          |      |
| Total PAH                       | 42.3                   | 40.6            | 40.8         |      |
| EcoChem CEM                     | NO <sup>a</sup>        | 33.2            | 39.0         |      |
| High Concentration Test         |                        |                 |              |      |
| Naphthalene                     | 97.0                   | NP <sup>b</sup> | NP           |      |
| Phenanthrene                    | 91.4                   | NP              | NP           |      |
| Pyrene                          | 68.2                   | NP              | NP           |      |
| Total PAH                       | 256.6                  | NP              | NP           |      |
| EcoChem CEM                     | NO                     | NO              | NO           |      |

<sup>a</sup>NO=Not operational.<sup>b</sup>NP=Not performed.<sup>c</sup>NC=Not calculated.**Table 12.** Measured Flue Gas Concentrations for the Test of the SNL and Metorex CEMs at the Low Metals Concentrations

| Metal          | Concentration, µg/dscm |                 |         |              |     |         |              |     |         |
|----------------|------------------------|-----------------|---------|--------------|-----|---------|--------------|-----|---------|
|                | 1st Daily RM           |                 |         | 2nd Daily RM |     |         | 3rd Daily RM |     |         |
|                | RM                     | SNL             | Metorex | RM           | SNL | Metorex | RM           | SNL | Metorex |
| Antimony (Sb)  | 4.5                    | ND <sup>a</sup> | ND      | 5.1          | ND  | ND      | 4.5          | ND  | 5.13    |
| Arsenic (As)   | 4.4                    | ND              | 3.65    | 3.8          | ND  | 0.83    | 3.6          | ND  | 1.19    |
| Barium (Ba)    | 11.7                   | ND              | ND      | 15.8         | ND  | ND      | 18.6         | ND  | 6.23    |
| Cadmium (Cd)   | 9.7                    | ND              | 2.63    | 12.1         | ND  | ND      | 13.2         | ND  | 10.02   |
| Chromium (Cr)  | 22.3                   | ND              | 2.49    | 23.5         | ND  | 0.56    | 28.0         | ND  | 22.29   |
| Cobalt (Co)    | 7.8                    | ND              | 12.11   | 7.1          | ND  | ND      | 7.1          | ND  | 14.68   |
| Lead (Pb)      | 101                    | ND              | 11.51   | 85.6         | ND  | 9.06    | 110          | ND  | 12.36   |
| Manganese (Mn) | 21.8                   | ND              | 5.89    | 29.2         | ND  | ND      | 31.6         | ND  | 19.43   |
| Nickel (Ni)    | 39.6                   | ND              | 27.52   | 29.1         | ND  | 6.15    | 42.4         | ND  | 21.87   |
| Selenium (Se)  | 11.4                   | ND              | 1.51    | 12.3         | ND  | 1.47    | 12.3         | ND  | 3.62    |
| Thallium (Tl)  | 1.1                    | ND              | ND      | 1.5          | ND  | ND      | 1.7          | ND  | ND      |

<sup>a</sup>ND=Not detected.

EcoChem CEM were 527% and 99%. As was seen in the VOC CEM tests, the RA at the higher test flue gas concentration was improved in comparison to the lower test concentration.

### Multi-Metal CEM Tests

Tables 12 through 14 summarize the results of the three sequential RM measurements performed each test day and compares these to the Sandia National Laboratories (SNL) and Metorex CEM

measurements. Neither CEM measured beryllium or mercury, so these metals are not included in the three tables. In addition, results for silver are not included in the tables. Spike recovery from QA samples was poor, so silver concentra-



**Table 13.** Measured Flue Gas Concentrations for the Test of the SNL and Metorex CEMs at the Intermediate Metals Concentrations

| Metal          | Concentration, µg/dscm |                 |         |                    |     |         |                    |     |         |
|----------------|------------------------|-----------------|---------|--------------------|-----|---------|--------------------|-----|---------|
|                | Reference Method 1     |                 |         | Reference Method 2 |     |         | Reference Method 3 |     |         |
|                | RM                     | SNL             | Metorex | RM                 | SNL | Metorex | RM                 | SNL | Metorex |
| Antimony (Sb)  | 11.0                   | ND <sup>a</sup> | 39.73   | 11.6               | ND  | 22.00   | 9.5                | ND  | 8.49    |
| Arsenic (As)   | 11.1                   | 63              | 11.92   | 10.8               | 42  | 0.74    | 8.7                | 115 | 6.61    |
| Barium (Ba)    | 78.0                   | 251             | 44.37   | 80.0               | 199 | 11.87   | 49.2               | 463 | 9.92    |
| Cadmium (Cd)   | 14.0                   | ND              | 7.22    | 15.0               | ND  | 26.93   | 14.2               | ND  | 10.09   |
| Chromium (Cr)  | 54.7                   | ND              | 56.48   | 59.5               | ND  | 72.51   | 50.3               | ND  | 25.68   |
| Cobalt (Co)    | 32.3                   | ND              | 14.72   | 33.9               | ND  | 20.79   | 27.4               | ND  | 9.79    |
| Lead (Pb)      | 141                    | 144             | 107.07  | 141                | 93  | 51.80   | 136                | 106 | 40.86   |
| Manganese (Mn) | 24.2                   | ND              | 61.4    | 24.6               | ND  | 55.58   | 18.2               | ND  | 31.25   |
| Nickel (Ni)    | 59.9                   | ND              | 26.48   | 61.2               | ND  | 21.26   | 52.6               | ND  | 15.76   |
| Selenium (Se)  | 43.2                   | ND              | 29.34   | 54.5               | ND  | 21.27   | 53.2               | ND  | 18.12   |
| Thallium (Tl)  | 11.1                   | ND              | 12.96   | 11.2               | ND  | 4.49    | 12.4               | ND  | 2.72    |

<sup>a</sup>ND=Not detected.**Table 14.** Measured Flue Gas Concentrations for the Test of the SNL and Metorex CEMs at the High Metals Concentrations

| Metal          | Concentration, µg/dscm |     |         |                    |                 |         |                    |     |         |
|----------------|------------------------|-----|---------|--------------------|-----------------|---------|--------------------|-----|---------|
|                | Reference Method 1     |     |         | Reference Method 2 |                 |         | Reference Method 3 |     |         |
|                | RM                     | SNL | Metorex | RM                 | SNL             | Metorex | RM                 | SNL | Metorex |
| Antimony (Sb)  | 114                    | 233 | 27.32   | 75.7               | 186             | 18.35   | 43.5               | 131 | 6.59    |
| Arsenic (As)   | 82.2                   | 75  | 21.82   | 64.8               | 86              | 13.28   | 54.8               | 65  | 4.68    |
| Barium (Ba)    | 331                    | 650 | 207.37  | 484.3              | ND <sup>a</sup> | 111.07  | 285                | ND  | 27.29   |
| Cadmium (Cd)   | 88.0                   | ND  | 33.58   | 60.9               | ND              | 31.73   | 88.7               | ND  | 22.18   |
| Chromium (Cr)  | 425                    | ND  | 129.33  | 299                | ND              | 91.85   | 241                | ND  | 34.70   |
| Cobalt (Co)    | 357                    | ND  | 100.16  | 229                | ND              | 67.47   | 248                | ND  | 37.62   |
| Lead (Pb)      | 1,650                  | ND  | 297.20  | 1,082              | ND              | 282.71  | 2,176              | 54  | 167.04  |
| Manganese (Mn) | 179                    | ND  | 52.89   | 89.9               | ND              | 35.25   | 95.6               | ND  | 16.56   |
| Nickel (Ni)    | 550                    | ND  | 160.10  | 347                | ND              | 111.42  | 429                | ND  | 67.89   |
| Selenium (Se)  | 421                    | ND  | 102.52  | 399                | ND              | 96.70   | 383                | ND  | 39.92   |
| Thallium (Tl)  | 114                    | ND  | 32.29   | 94.3               | ND              | 28.10   | 113                | ND  | 16.84   |

<sup>a</sup>ND=Not detected.

tions as measured by the RM are highly suspect. The SNL CEM did not detect any of the test trace metals on the low concentration test day, only arsenic, barium, and lead were reported on the intermediate concentration test day, and only antimony, arsenic, barium, and lead for one or more RM periods were reported on the high concentration test day.

The RAs corresponding to the measurement pair data in Tables 12 through

14 are summarized in Table 15. The data in Table 15 show that the RAs for the SNL CEM ranged from 64% to 1,560% for the three metals reported on the intermediate concentration test day, and from 65% to 188% for the two metals reported on the high concentration test day. RAs for the Metorex CEM ranged from 88% to 236%, with an average of 129% and a median of 116% for the low concentration test. Corresponding RAs for the interme-

diate concentration test were 72% to 467%, with an average of 168% and a median of 135%, and, for the high concentration test, 93% to 177%, with an average of 129% and a median of 121%. The RAs for the Metorex CEM were comparable for each test concentration. No marked improvement as flue gas concentration increased, as observed for the VOC CEMs, is seen in the Metorex CEM data.

**Table 15.** Relative Accuracies of the SNL and Metorex CEMs

| Metal                | RA, %              |              |            |                    |              |      |
|----------------------|--------------------|--------------|------------|--------------------|--------------|------|
|                      | SNL                |              |            | Metorex            |              |      |
|                      | Test Concentration |              |            | Test Concentration |              |      |
|                      | Low                | Intermediate | High       | Low                | Intermediate | High |
| Antimony (Sb)        | NC <sup>a</sup>    | NC           | 188        | NC                 | 467          | 158  |
| Arsenic (As)         | NC                 | 1,560        | 65         | 125                | 174          | 101  |
| Barium (Ba)          | NC                 | 905          | NC         | NC                 | 135          | 153  |
| Cadmium (Cd)         | NC                 | NC           | NC         | 89                 | 177          | 123  |
| Chromium (Cr)        | NC                 | NC           | NC         | 158                | 94           | 113  |
| Cobalt (Co)          | NC                 | NC           | NC         | 236                | 72           | 118  |
| Lead (Pb)            | NC                 | 64           | NC         | 115                | 112          | 177  |
| Manganese (Mn)       | NC                 | NC           | NC         | 116                | 261          | 146  |
| Nickel (Ni)          | NC                 | NC           | NC         | 88                 | 77           | 121  |
| Selenium (Se)        | NC                 | NC           | NC         | 104                | 113          | 93   |
| Thallium (Tl)        | NC                 | NC           | NC         | NC                 | 171          | 111  |
| Average <sup>b</sup> | —                  | 843          | 127        | 129                | 168          | 129  |
| Median <sup>b</sup>  | —                  | 905          | 65,<br>188 | 116                | 135          | 121  |

<sup>a</sup>NC=Not calculated.<sup>b</sup>Average and median exclude RAs NC.**Mercury CEM Tests**

Table 16 summarizes the results of three sequential RM measurements performed each mercury CEM test day and compares these to the corresponding three mercury CEM measurements. Calculated RAs for each CEM are also given in the table for the three test days, each representing a different flue gas mercury concentration. The table indicates several periods during which the Perkin-Elmer and the Senova CEMs were not in operation.

The data in Table 16 show that the EcoChem CEM had an RA of about 60% for both the low and the high concentration tests. The RA at the intermediate concentration was increased, at 92%. The RA of the Perkin-Elmer CEM was 602% at the low mercury concentration and 1,150% (based on two measurement pairs) at the intermediate mercury concentration. The RA of the Senova CEM was 186% at the one test concentration having data.

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**Table 16.** Measured Flue Gas Concentrations and RAs for the Mercury CEM Tests

| Test                                      | Mercury Concentration, $\mu\text{g/dscm}$ |             |                  |                 |
|---|---|-------------|------------------|-----------------|
|   | RM  | EcoChem CEM | Perkin-Elmer CEM | Senova CEM      |
| <b>Low Mercury Concentration</b>          |   |             |                  |                 |
| RM 1                                      | 21  | 22          | 78               | NO <sup>a</sup> |
| RM 2                                      | 16  | 20          | 42               | NO              |
| RM 3                                      | 13  | 19          | 11               | NO              |
| RA, %                                     |   | 60          | 602              | NC <sup>b</sup> |
| <b>Intermediate Mercury Concentration</b> |   |             |                  |                 |
| RM 1                                      | 56  | 83          | 61               | NO              |
| RM 2                                      | 34  | 43          | NO               | NO              |
| RM 3                                      | 40  | 56          | 125              | NO              |
| RA, %                                     |   | 92          | 1,150            | NC              |
| <b>High Mercury Concentration</b>         |   |             |                  |                 |
| RM 1                                      | 119                                       | 137         | NO               | 232             |
| RM 2                                      | 94  | 81          | NO               | 116             |
| RM 3                                      | 86  | 62          | 405              | 165             |
| RA, %                                     |   | 61          | NC               | 186             |

<sup>a</sup>NO=Not operational.<sup>b</sup>NC=Not calculated.

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