



Project Summary

Field Evaluation of Carbon Monoxide and Hydrogen Sulfide Continuous Emission Monitors at an Oil Refinery

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An eleven-month field evaluation was conducted for five hydrogen sulfide and four carbon monoxide continuous emission monitors (CEMs). The H₂S CEMs were installed on a fuel gas line and the CO CEMs were installed on a stack from a fluidized bed catalytic cracking unit at a refinery. Performance specification testing was routinely performed on the instruments as they were operated and maintained in this field environment.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, 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

On March 15, 1978, EPA promulgated New Source Performance Standards (NSPS) that required petroleum refineries to continuously monitor the carbon monoxide (CO) emissions from fluid catalytic cracking (FCC) units.¹ Refineries were required also to continuously monitor either the hydrogen sulfide (H₂S) concentration in fuel gas feed lines or the sulfur dioxide (SO₂) concentration in the exhaust of the boiler burning the fuel gas. However, refineries were not required to install H₂S or CO continuous emission monitors (CEMs) until performance specifications for the instruments were published by the EPA.

In April 1979, the EPA initiated work to establish these specifications and also to determine the durability, maintenance requirements, and data validity of commercially available CO and H₂S continuous emission monitors. To procure the monitors, 35 vendors of commercially available stack gas monitors for CO and H₂S were asked to recommend monitors for evaluation. Sixteen did not respond. A total of ten H₂S and thirteen CO monitors were advanced for consideration. From this list, five H₂S and four CO monitors were selected for evaluation (Table 1). The selection criteria included operating principle, engineering judgment about suitability for use at petroleum refineries, and total cost.

These nine monitors were installed in a trailer at the Harmon Engineering & Testing facility in Auburn, Alabama and then transported to a petroleum refinery for an eleven-month field evaluation. Here, the H₂S monitors measured the H₂S concentration in a fuel gas at a point downstream of an amine treater (an H₂S control device) and the CO monitors measured the CO concentration in the exhaust gas from a boiler on an FCC unit. An EPA-designed stack gas conditioning system removed particulate and water from the FCC stack gas at the sampling port before sending the clean, dry gas to a manifold in the trailer (where it was distributed to the monitors). A similar manifold was used to distribute fuel gas to the H₂S monitors.

Table 1. Continuous Emission Monitors Evaluated

<i>Instrument Manufacturer</i>	<i>Model Number</i>	<i>Abbreviation</i>	<i>Operating Principle</i>
CARBON MONOXIDE ANALYZERS			
<i>Anarad, Inc. Santa Barbara, CA P.O. Box 3180 Santa Barbara, CA 93105</i>	<i>501R</i>	<i>Anarad</i>	<i>Nondispersive Infrared Detector (NDIR)</i>
<i>Ecolyzer Energetics Science 85 Executive Blvd. Elmsford, NY 10523</i>	<i>3107/2949</i>	<i>Ecolyzer</i>	<i>Electrochemical Sensor</i>
<i>Applied Automation, Inc. Pawhuska Road Bartlesville, OK 74004</i>	<i>Optichrom 102</i>	<i>AA102</i>	<i>Gas Chromatograph/Flame Ionization Detector (GC/FID)</i>
<i>Mine Safety Appliances Company 7522 Neade Street Pittsburgh, PA 15208</i>	<i>LIRA 202</i>	<i>MSA</i>	<i>Nondispersive Infrared/Luft Detector (NDIR/Luft)</i>
HYDROGEN SULFIDE ANALYZERS			
<i>Bendix Corporation Environmental and Process Instruments P.O. Drawer 831 Lewisburg, WVA 24901</i>	<i>7770</i>	<i>Bendix</i>	<i>Gas Chromatograph/Flame Photometric Detector (GC/FPD)</i>
<i>Del Mar Scientific, Inc. P.O. Box 486 Addison, TX</i>	<i>DM-W</i>	<i>Del Mar</i>	<i>Lead Acetate Impregnated Paper Tape</i>
<i>Houston Atlas, Inc. 9441 Baythorne Drive Houston, TX 77041</i>	<i>825R/102</i>	<i>HAI</i>	<i>Lead Acetate Impregnated Paper Tape</i>
<i>Process Analyzers, Inc. 1101 State Road Princeton, NJ 08540</i>	<i>32-230</i>	<i>PAI</i>	<i>Gas Chromatograph/Flame Photometric Detector (GC/FPD)</i>
<i>Teledyne Analytical Instruments 333 W. Mission Avenue San Gabriel, CA 91776</i>	<i>611 DMCO-20X</i>	<i>Teledyne</i>	<i>Ultraviolet Absorption</i>

The output from the monitors was recorded on an Esterline Angus PD 2064 data logger, Techtran 816 tape cassette recorder and an Esterline Angus multipoint recorder. The multipoint recorder printed the instantaneous monitor value at 3-minute intervals. The PD 2064 read the monitors' output at 3-minute intervals and printed the average after ten readings, except during relative accuracy tests when it read it every minute and printed the average of 30 readings. The PD 2064 also initiated daily zero and span checks of the monitors with calibration gases and recorded the results.

Periodic tests for relative accuracy, calibration error and short- and long-term drift were conducted periodically during the field evaluation. EPA Method 11 was the reference method for the relative accuracy tests on the H₂S monitors.

EPA Method 10 (NDIR) and a colorimetric method (leuco crystal violet, LCV) being evaluated during this study, were the reference methods for the relative accuracy tests on the CO monitors.

The results of the monitor evaluation are summarized here. A full report describes the test results, the LCV analytical method, and the components and performance of the FCC stack gas conditioning system.

Results and Discussions **Carbon Monoxide CEMs**

Initially, the monitor evaluation was intended to determine the ability of CO and H₂S monitors to meet some tentative performance specifications similar to those for NO_x and SO₂ CEMs. However, after the study was initiated, EPA revised Performance Specification 2

(NO_x and SO_x monitors) to require only calibration error (CE) and relative accuracy (RA) tests for certification.² Since similar requirements were expected to apply to CO and H₂S monitors, the focus of the field evaluation shifted to concentrate on just these two requirements.

Table 2 summarizes the relative accuracy results obtained on the CO monitors. Overall, four valid relative accuracy tests were conducted on the CO monitors. In these tests, the reference method samples were collected in Tedlar bags preceded by an alkaline potassium permanganate solution for NO_x/SO_x removal and sent to the EPA laboratory at Research Triangle Park, North Carolina, for analysis by Method 10 and the LCV method.

Since the MSA and Anarad monitors suffered interference from CO₂, a cylin-

Table 2. Summary of CO Relative Accuracy Tests at Refinery

Date	Number of Reference Method Samples	Mean CO ₂ Conc (%)	LCV ^a CO Conc (ppm)	Relative Accuracy					
				Ecolyzer		Anarad ^b		MSA ^b	
				% Std ^c	% [CO]	% Std ^c	% [CO]	% Std ^c	% [CO]
9/80	5	2	80	5	34	3.8	24	2.9	18.4
1/81	9	2	404	14	17	13	16	13	16
2/81 (A)	9	12	507 ^d	>100	>100	7.7	7.6	4.2	4.3
2/81 (B)	9	3	712	^e	^e	12.7	8.9	9.7	6.8
Mean				40	50	9.3	14	7.4	11

^a This is the average of the manual method results using the leuco crystal violet method developed in this study.

^b Corrected for CO₂ interference.

^c Standard for CO: 500 ppm.

^d Monitors sampled cylinder gases containing 502 ppm CO, 12% CO₂ and different concentrations of NO and SO₂ in nitrogen. This was done to evaluate the performance of the monitors when they were sampling a stack gas with NO_x and SO₂ levels representative of an FCC stack gas. During the 11-month study, process upsets and refinery equipment malfunction caused the CO levels to exceed the span range of the monitors and so it was necessary to dilute the stack gas to bring the CO level into the working range of the monitors during the relative accuracy test. Dilution was obtained by introducing plant instrument air at the probe. This dilution reduced the NO_x and SO₂ levels by a factor of 4 to 6 and permitted the Ecolyzer to obtain an accurate analysis of the stack gas.

^e Monitor not operational because of detector failure from high SO₂ and NO levels encountered in Test 2/81(A).

der gas containing 10% CO₂ in nitrogen was introduced at the manifold after each relative accuracy test and the monitor's response (ppm CO/1% CO₂) was used to correct the relative accuracy test results for the CO₂ content of the stack gas. As expected, the CO₂ interference remained quite steady during the study (Anarad, 3 ppm/1% CO₂, MSA 1 ppm/1% CO₂).

Table 3 summarizes the results of the calibration drift (CD) tests. These tests were performed in conjunction with the daily zero and span checks. Since the instruments were not zeroed each day, the values reported represent the daily zero drift values corrected for the zero value recorded for the start of the 24-hour period.

The Applied Automation performed well during the laboratory check-out, but suffered from an unknown interference in the FCC gas sample. A valid relative accuracy test was not completed because of this and because of the erratic performance of the instrument. Testing of the instrument was discontinued after a factory representative was unable to find the cause of the interference and unable to correct the erratic behavior in the monitor's output.

The Model 2949 NO_x/SO_x scrubber supplied with the Ecolyzer was found to be inadequate for long-term use of FCC stack gases where SO₂ levels of 400-800 ppm and NO_x levels of 100-400 ppm are encountered. Because some of the scrubbers were exhausted within

Table 3. Calibration Drift Test Results for CO Monitors

Day	Calibration Drift ^{a, b} (%)					
	Ecolyzer		Anarad		MSA	
	Zero	Span	Zero	Span	Zero	Span
Test 1						
1	1.4	0.4	1.7	0.1	0.6	0.1
2	0.3	4.4	0.2	2.4	0.9	1.2
3	0.2	1.7	0.2	1.6	1.2	2.0
4	0.6	1.0	1.0	0.2	1.4	0.8
5	0.4	0.7	2.0	0.8	2.5	6.2
6	0.9	0.9	2.1	1.5	3.3	3.0
7	1.2	1.6	3.2	4.5	2.9	0
Test 2						
1	0.2	7.2	2.4	0.7	0	0.9
2	0.2	0.1	0.2	4.4	1.7	2.4
3 ^c	0.7	10.8	0.4	3.4	5.4	1.3
4	0.2	0.2	0.4	0.3	1.3	3.6
5	0	1.6	1.1	0.4	2.5	3.7
6	0.1	0.9	0.1	1.9	0.2	1.1
7	0.1	0.3	0.5	1.0	0.1	1.7
Test 3						
1	0.1	0.1	0.9	0.6	0.2	1.2
2	0.3	3.4	1.3	1.7	0.2	1.2
3	0	0.4	0	0.7	0.4	0.1
4	0.1	0.9	0.6	1.1	0.7	1.2
5	3.1	2.7	0.4	1.1	1.8	2.8
6	2.2	2.8	0.4	0.1	4.2	1.1
7	0.7	0.9	0.2	0.1	0.9	2.8

^a Values in table represent the daily drift as defined by the following equation

$$\frac{|\text{Calibration Gas Concentration} - \text{Monitor Reading}| \times 100\%}{\text{Monitor Span Value}}$$

^b Because long-term drift was of primary concern, the instruments were not zeroed daily. The values in the table have been corrected by the daily zero drift.

^c Instrument recalibration was performed this date.

24-hours, it was decided to use them only during relative accuracy tests. During routine unattended operation a 25 cm long × 2.5 cm ID PVC tube packed with activated charcoal was substituted for the 2949 scrubber. (This charcoal tube could not be used for RA tests, because it caused a 30-minute delay in the analyzer's response to a change in stack gas CO concentration.)

Throughout the field study, the FCC unit malfunctioned at frequent intervals, which caused the CO level in the stack to rise above the span range of the monitors (1000 ppm). Such malfunctions occurred during the first two relative accuracy tests and it was necessary to add ambient air to the stack gas at the probe exit to bring the CO concentration below 1000 ppm. Since this dilution significantly reduced the SO_x and NO_x levels in the sampled gas, the Ecolyzer performed better than expected during the test. (The actual effect of NO_x and SO_x on the Ecolyzer can be seen by referring to RA Test 3 (February 1981A) in Table 2—a test in which cylinder gases containing SO_x and NO_x at levels normally expected in an FCC stack gas were used instead of diluted stack gas.)

The Ecolyzer failed to complete the field study because of detector failure. The detector failed twice during the seven months the monitor operated. The monitor also experienced severe drift throughout this seven-month period.

Because its output was not compatible with the PD 2064 input requirements,

the MSA instrument was not operational until July 1980. The monitor performed well in all the relative accuracy tests after its response for CO₂ in the sampled gas was corrected. It suffered two major outages (both of which were corrected by optical realignment) after it passed the first relative accuracy test. Because of these outages and the late start up, the calibration error test could not be conducted on this monitor. There is no reason to suspect, however, that this monitor would not have passed this test. The monitor suffered from random short-term drift, but over the period of a month its drift averaged less than 3 percent of span. The percent uptime of the monitor was 86 percent.

The Anarad operated without malfunction from the time it was installed in the trailer (November 1979) until the project was completed in April, 1980. It performed well during the relative accuracy and calibration error tests. Like the MSA, it sometimes suffered from random short-term drift, but over the period of a month, its drift averaged less than 3 percent of span.

Hydrogen Sulfide CEMs

The agreement between the monitors and Method 11 changed radically during relative accuracy tests. Initially, the monitors showed a negative bias with respect to Method 11, but in early February a positive bias began to be observed. The agreement between the monitors and Method 11 sometimes

changed drastically from one day to the next. Tests to determine the cause of this bias were inconclusive. When two laboratories simultaneously measured the H₂S concentration in the fuel gas, the two laboratories agreed closely but their results were significantly different from that of the monitors (Table 4, RA Test 5). Further, when the fuel gas was spiked with known amounts of H₂S, both the monitors and the reference method recovered the spike. Thus, the cause of the bias remains unknown. Perhaps it resulted from a combination of several factors, including the slow response of the monitors and sudden changes of short duration in the H₂S concentration in the fuel gas.

Table 5 summarizes the results of the calibration drift (CD) tests. These tests were performed in conjunction with the daily zero and span checks. Since the instruments were not zeroed each day, the values reported represent the daily zero drift values corrected for the zero value recorded for the start of that 24-hour period. Specific comments about the monitors are presented below.

The Teledyne responded to many other compounds present in the fuel gas. The interferences were so severe that field evaluation was discontinued on the monitor. It was not possible to install a scrubber that would effectively remove the majority of the interferences before the instrument failed completely.

The PAI was not operational for more than two weeks despite being returned

Table 4. Summary of H₂S Relative Accuracy Tests at Refinery

Test Number	Start Date	Number of Reference Method Samples	Method 11 Mean H ₂ S Conc (ppm)	Relative Accuracy							
				Bendix		Houston Atlas		Del Mar		Teledyne	
				% std ^a	% [H ₂ S] ^a	% std ^a	% [H ₂ S] ^a	% std ^a	% [H ₂ S] ^a	% std ^a	% [H ₂ S] ^a
1	4/27/80	9	159	28.9	29.9	b	b	25.1	25.9	115	119
2	5/5/80	9	201	39	32	b	b	52.4	43.0	74	61
3	6/9/81	9	208	58.8	47.4	47.1	37.9	45.8	36.3	b	b
4A	1/20/81	9	190	18.5	16.1	13.8	12.0	28.4	24.7	b	b
4B	1/20/81	9	197	16.4	13.7	30.0	25.1	48.9	40.9	b	b
5	2/18/81										
	Lab 1	9	34.6	18.1	86.4	24.4	116	32.0	153	b	b
	Lab 2	7	31.7	22.4	117	28.9	148	39.4	205	b	b
6	2/25/81 ^d	6	150	11.1	12.2	c	c	c	c	b	b
7	2/25/81	8	138	33.5	40.2	c	c	c	c	b	b
8	3/31/81 ^d	10	114	8.3	12.0	b	b	21.5	31.1	b	b

^a Standard 165 ppm H₂S, [H₂S] = Method 11 result.

^b Monitor not operational.

^c Monitor operational but not included in test because it could not be brought into calibration.

^d Fuel gas spiked with known amount of H₂S using Houston Atlas, Inc. Model 601 diluter.

Table 5. Calibration Drift Test Results for H₂S Monitors

Test Number	Calibration Drift ^{a, b} (%)					
	Bendix		Houston Atlas		Del Mar	
	Zero	Span	Zero	Span	Zero	Span
Test 1						
1	0	0.7	0.1	6.3	12.5	21.3
2	0	0.7	0.3	4.5	9.6	30.9
3	0	1.1	0.4	0.3	19.5	52.6
4	0	1.1	0.1	1.0	0.7	101
5	0.1	9.2	0.3	13.9	4.8	44.0
6	0.1	8.1	0.1	13.9	0	3.3
7	0	0.7	6.9	2.9	2.6	8.1
Test 2						
1	0	1.1	3.5	10.8	6.6	34.2
2	0	0	1.4	26.0	4.4	26.5
3	0	0.7	4.5	3.5	1.5	2.6
4	0.2	0.4	4.2	3.1	1.5	2.6
5	0.1	2.6	1.0	12.8	1.5	1.8
6	1.0	1.1	0.6	1.4	0	0
7	0.1	0.4	—	11.5	4.0	4.8
Test 3						
1	0.1	1.8	0.1	4.9	1.1	7.4
2	1.0	0.7	0.3	1.0	0.4	6.6
3	0.2	0.7	1.7	15.6	1.1	8.5
4	0.2	1.5	5.2	21.5	10.7	6.6
5	0.1	1.5	7.6	—	9.9	18.4
6	4.2	2.9	5.9	4.9	0	6.3
7	4.2	4.0	2.1	5.2	1.5	3.7
Test 4						
1	0	0.7	3.1	3.8	0.4	1.1
2	0	0	0.7	6.6	0.7	3.7
3	0	0.7	0.7	0.7	0	0
4	0	0	0	0.7	0.6	4.8
5	0	0	0	6.6	2.0	12.1
6	0	0.4	0	0	—	—
7	—	—	0.3	10.4	—	—

^a Values in table represent the daily drift as defined by the following equation

$$\frac{\text{Calibration Gas Concentration} - \text{Monitor Reading}}{\text{Monitor Span Value}} \times 100\%$$

^b Because long-term drift was of primary concern, the instruments were not zeroed daily. The values in the table have been corrected by the daily zero drift.

to the manufacturer three times for repairs. A successful relative accuracy test was never obtained.

The Bendix operated continuously from the initial start-up until final shut-down with only four brief outages. No interferences were detected during initial check-out; a possible negative interference in the fuel gas was indicated but not confirmed. This instrument experienced the least amount of drift of any of the CEMs.

One problem encountered with this instrument resulted from the fact that it only sampled the fuel gas approximately once every 3.5 minutes. This feature of

the Bendix makes comparing its output for 30 minutes (total sample collection time less the 10 seconds) to the results of a 30-minute Method 11 sample of dubious validity. This is particularly true when one considers the sudden changes that can occur in the H₂S level of the fuel gas. The Bendix did complete the field study with only two major outages and had a percent uptime of 89 percent.

The Houston Atlas suffered frequent mechanical failure but did complete the majority of the field testing. Its percentage uptime was 76 percent. The failures were primarily in the sample dilution system which employs a Teflon sliding

block containing a cavity of known volume. At times, the instrument suffered from excessive drift. Calibration usually took at least four hours.

The Del Mar operated for the entire test program without mechanical failure. However, because rotameters were used to achieve a dilution of the fuel gas prior to analysis, its calibration changed when the density and viscosity of the fuel gas changed. This fact caused the instrument to have a significant amount of drift. The percent uptime was 97 percent, the highest of any of the monitors.

Conclusions and Recommendations

The Anarad and MSA successfully completed the eleven-month field study and demonstrated that reliable CO monitors with good drift control are available for use at petroleum refineries. Although CO₂ is an interference with these monitors, its effect is small (in terms of the span range) and correctable. Water vapor will also interfere with these NDIR instruments, but it is unlikely that these instruments would sample a gas stream that had not already had the moisture removed.

Overall, the performance of the five H₂S monitors was disappointing. Two of the five monitors never obtained a valid sample and a third suffered frequent malfunction. The absolute agreement between Method 11 and all monitors was poor and variable in eight of the ten relative accuracy tests. Since the source of this difference is unknown, the use of H₂S monitors for compliance purposes cannot be recommended at this time nor can we advance performance specifications for accuracy. However, these monitors may be useful for determining trends and for indicating the monthly performance of the amine treater. For example, the average H₂S concentration for all Method 11 tests (140 ppm) compares reasonably well with the average for each monitor: Del Mar (133 ppm), Houston Atlas (130 ppm) and Bendix (119 ppm).

References

1. Performance Standards for New Stationary Sources, *Federal Register*, 43: 10869, March 15, 1978.
2. Proposed Revisions to Performance Specifications 2 and 3, *Federal Register*, 46: 8359, January 26, 1981.

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The complete report, entitled "Field Evaluation of Carbon Monoxide and Hydrogen Sulfide Continuous Emission Monitors at an Oil Refinery," (Order No. PB 82-227 406; Cost: \$12.00, subject to change) will be available only from:

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