⌀EPA Project Summary

Evaluation of HCl Continuous Emission Monitors

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The final report summarized herein presents the findings obtained from the field evaluation of commercially available HCl monitoring equipment at a municipal waste-fired boiler not equipped with HCl emission control equipment. The analyzers were operated continuously during a two-month test period.

The measurement techniques employed by the evaluated HCl monitors were IR gas filter correlation, specific ion electrode, wet chemical colorimetric, dry reaction colorimetric, and gas membrane galvanic cell.

Except for the gas membrane galvanic cell monitor, the HCl monitoring equipment produced effluent measurements in good agreement with concurrent reference measurements. The results comparing the CEM data to the reference wet-chemistry measurement data indicate no biases in any of the monitor measurement techniques resulting from analytical interferences present in the effluent of this municipal refuse-fired boiler. Further, both in-stack dilution systems and the nondilution, heat-traced sampling system were found to reliably provide representative effluent samples to the analyzers.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment 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

Certain U.S. Environmental Protection Agency (EPA) regulations (40 CFR 264, Subpart 0, Sections 264.340 - 264.351) suggest that hazardous waste incineration facilities must monitor HCl on a continuous basis to economically demonstrate continuous compliance with the HCl emissions requirement of Section 264.343(b). Already, California and certain northeastern states (e.g.,Connecticut, Massachusetts, New York, New Jersey, and Pennsylvania) already require operating permits for new or proposed refuse-fired boilers to include a provision that HCl continuous emission monitors (CEMs) be installed and operated to demonstrate HCl removal requirements when HCl CEM systems become commercially available. However, not yet documented are identification of the various types of commercially available HCl CEMs or the demonstration of their effectiveness in continuous monitoring effluent HCl emissions from hazardous waste incinerators or from refuse-fired boilers.

The Quality Assurance Division (QAD) of the Environmental Monitoring Systems Laboratory (EMSL), Research Triangle Park, North Carolina, is responsible for assessment of environmental monitoring technologies and systems. QAD has initiated a field test program to assess the performance of commercially available HCl CEMs. The major objectives of the project were (1) to evaluate the reliability of multiple HCl analyzers in terms of the accuracy, precision, and availability of measurement data, and (2) to determine the adequacy of sampling

systems for reliably providing effluent samples to the various HCl analyzers.

The field evaluation was conducted at a municipal refuse-fired boiler with HCl effluent concentrations ranging, typically, between 200 and 500 ppm.

The sampling location was the outlet duct from the electrostatic precipitator (ESP). Six HCl analyzers, involving four different detection techniques and three sampling systems, were evaluated. Table 1 presents information concerning the specific analyzers/monitoring systems selected for evaluation. The reader will note that the analyzers manufactured by MDA Scientific, Lear Siegler Instruments (LSI) and CEA Instruments, designed for ambient air applications, are not equipped with a sample conditioning/ handling system.

Test Procedures

The field evaluation utilized concurrent operations of the various analyzers and sampling systems to determine factors affecting the reliability of the equipment. Performance tests for relative accuracy, calibration drift, calibration error, and response time were conducted according to procedures outlined in "Gaseous Continuous Emission Monitoring Systems - Performance Specification Guidelines for SO_2, NO_2, CO_2, and TRS," EPA-450/3-82-026, October 1982. Manual sampling, using a wet-chemical impinger sampling train, was also conducted. To facilitate quantification of HCl sample line losses, flue gas sampling was conducted simultaneously at two locations - the duct and the CEMs' common manifold. The manifold distributed diluted flue gas sample to the CEMs delivered from one of the two dilution probes located at the duct.

The HCl in the flue gas samples was collected with a sampling train similar to an EPA Reference Method 6 train. The absorbing reagent, 15 mL of 0.1 N NaOH, was added to each of the first two impingers. The reagent was used in the manifold impinger trains at 0.001 N NaOH because of the lower HCl content after dilution by the dilution probe. The third impinger (a Mae West design) was filled with calcium sulfate (Drierite) to protect the Singer dry gas meter from moisture. The desired sampling rate during the relative accuracy testing was 2 L/min with a sampling time of 20 min.

The sampling systems used for the duct sample consisted of all-glass components that contacted the stack gases. A glass-lined probe and glass components were used to convey the stack gas to the duct impinger train. A three-way glass valve was mounted in-line directly upstream of the first impinger.

The techniques used for analysis of impinger samples were a mercuric nitrate titration procedure (EPA Method 325.3 - Method for Chemical Analysis of Water and Waste, EPA 600/4-79-020) and ion chromatography (IC). The mercuric nitrate titration procedure was used for analysis of samples in the field to provide rapid feedback on the operation of the HCl CEMs. The IC analysis was restricted to the laboratory and provided confirmation of the titration results.

At the beginning of each test period, all CEMs were calibrated (at zero and one upscale calibration point) to the same standard. Triplicate sampling and analysis, using wet-chemical impinger sampling and mercuric-nitrate titrations, were conducted on the calibration gases to verify their concentrations. The three analyzers not supplied with a probe and sample conditioning/ handling system (i.e., the LSI, MDA, and CEA analyzers were supplied gas samples from either the TECO or Compur dilution systems.

Results And Discussion

Operational problems were experienced at the startup of the analyzers and monitoring systems. The test personnel and equipment vendors spent the first few months of the field evaluation identifying and resolving problems affecting the reliability of HCl monitor operation.

The CEA Model TGA-410 HCl analyzer, initially provided for the field evaluation, did not respond to changes in sample concentration. CEA representatives suspected a bad electrochemical gas sensor within the analyzer and replaced the analyzer. However, the new analyzer performed similarly to the one replaced. As a result, CEA withdrew its analyzer from the evaluation.

Evaluation results, generally, indicate acceptable HCl CEM performance during the relative accuracy test periods. Wet chemical impinger sampling was conducted to collect "reference" HCl concentration measurements to compare to the HCl monitoring measurements so that relative accuracy could be determined. The computations of relative accuracy were performed using the procedures in Performance Specification 2, 40 CFR 60 Appendix B. A relative accuracy specification

Table 1.   *HCl Continuous Emission Monitors*

Manufacturer	Model	Measurement Technique	Sampling System	Measurement Ranges	Available Calibration Techniques
Thermo Electron instruments (TECO)	15	NDIR gas filter correlation	Dilution probe	Variable ranges from 0-5 ppm to 0-5000 ppm	Cylinder gases
MDA Scientific, Inc.	Series 7100	Colorimetric (chemically-treated cassette tape)	None	0-100 ppm or less	Stain card, cylinder gases
Lear Siegler Instruments (LSI)	TGM-555	Colorimetric (liquid reagent)	None	0-50 ppm or less	Liquid standards, cylinder gases
Compur	4150	Ion-sensitive electrode	Dilution probe	0-3353 ppm	Liquid standards, cylinder gases
CEA Instruments	TGA-410	Gas membrane galvanic cell	None	0-50 ppm or less	Liquid standards, cylinder gases
Bodenseewerk (BSWK)	677 IR	NDIR gas filter correlation	Heated probe, sampling line, and sampling pump to heated gas cell	0-1000 ppm	Cylinder gases, internal sealed-gas cell

ation of ≤ 20% was adopted for this evaluation. CEM wet-basis measurement data were corrected to dry-basis so that a direct comparison could be made to the dry-basis impinger results.

Table 2 presents the relative accuracy results for each of the CEMs.

Other findings from the relative accuracy determinations, not shown in Table 2, are briefly described below:

• The results of the calibration checks did not always indicate monitor performance during the relative accuracy tests. In each of the four cases where the relative accuracy result exceeded the ≤ 20% specification, the magnitude of the mean difference term indicated the reason for exceeding the specification may have been caused by an improper adjustment to the analyzer calibration. In two of these four cases, there was good agreement between the calibration gas values and the CEM responses to the calibration gas injections. In one case, the calibration check results were not consistent with the relative accuracy mean difference term (i.e., positive drift was noted from the post-test calibration check, but the relative accuracy mean difference term indicated a negative bias in the flue gas measurement). On one occasion, a significant amount of drift was noted (3.7% relative to instrument span, or 29% relative to the pre-test response), whereas the relative accuracy result (7.4%) indicated acceptable monitor performance.

• The relative accuracy results indicate that any effects of HCl line losses can be minimized by injecting the HCl calibration gases through the entire sampling system when performing dynamic calibrations.

• During the final relative accuracy test conducted on April 29, 1987, the sampling rate for the last five manifold impinger samples was reduced from 2 L/min (the prescribed sampling rate) to 1 L/min to determine if the sample flow rate had an effect on the results.

Significantly lower impinger sample results were produced at the lower sampling rate. The stainless steel hardware mounted on the manifold could possibly have contributed to these lower impinger sample values by adsorbing HCl at the lower flow rate.

A seven-day calibration drift evaluation was not performed according to the procedures of promulgated Performance Specification 2. However, daily calibration checks were performed over 3- and 4-day periods according to the calibration drift test procedures. These test data were compiled to demonstrate the capabilities of these HCl analyzers to maintain daily drift within the 2.5% of span specification of Performance Specification 2 adopted for this evaluation.

Table 3 presents the maximum daily calibration drift observed for each of the analyzers.

The calibration drift test was conducted on the Bodenseewerk monitoring system for seven consecutive days by using the data afforded by the automatic calibration check the Bodenseewerk performs using zero air and the internal gas-filled cell. This procedure did not require test personnel to remain on-site for seven consecutive days.

The calibration drift data indicate that the MDA and Compur analyzers may have difficulty producing repeatable results to satisfy the adopted calibration drift requirement.

Calibration error determinations were performed on four of the five monitors. The calibration error test procedure involved performing five nonconsecutive injections of the zero air and two HCl calibration gases through the entire monitoring system. The differences between the monitor responses and the known concentrations of the calibration gases were recorded. The calibration error determinations were computed by summing the absolute value of the mean difference and the 95% confidence interval determined for the five injections. Table 4 presents a comparison of the monitor calibration error determinations

conducted on the two dilution sampling systems. The Bodenseewerk monitoring system did not undergo a calibration error test because only one of the available HCl calibration gases (the 503 ppm cylinder gas) was within the 0-1000 ppm operating range of the analyzer. Periodic injections of the single gas yielded responses that were in excellent agreement with the gas value.

The following observations can be made from the results:

• Most of the calibration error results exceeded the ≤ 5% specification adopted for this evaluation. All the CEM responses to the 503 ppm gas, except for one MDA response, were within ± 8% of the cylinder gas value. For comparison purposes, all the monitors produced responses to the 503 ppm gas injections that would meet the Appendix F, Procedure 1 acceptable accuracy requirement of ± 15% using the Cylinder Gas Audit (CGA) procedure. The CGA procedure requires three gas injections of each of two audit gases and specifies that the average of the three responses should be used in determining accuracy. Monitor imprecision is not accounted for because the confidence interval is not included in the Procedure 1 accuracy determination.

• Because the LSI and MDA analyzers were calibrated to the 503 ppm HCl calibration gas, the LSI and MDA results for the high-level check (1556 ppm) are excessive as a result of the nonlinearity associated with the measurement techniques of these two monitors.

• The magnitude of the confidence interval terms for some of the analyzers reflects a high degree of monitor imprecision during these tests. These analyzers had difficulty producing repeatable responses to the same calibration gas. This same problem also affected the daily calibration drift results.

The response time is defined as the amount of time required for the meas-

Table 2. Summary of Relative Accuracy Determinations

| Test Date | Relative Accuracy Results | | | | |
	LSI	BSWK	TECO	MDA	Compur
3/19/87	4	8	9	27	13
3/20/87	24	14	31	6	8
4/27/87	17	6	19	4	23
4/29/87	8	3	4	7	11

Table 3. Summary of Maximum Daily Calibration Drift*

Analyzer	Low Range	High Range
LSI	2.2% (0/14)	4.2% (1/14)
Bodenseewerk	0.3% (0/10)	0.7% (0/10)
TECO	1.3% (0/15)	1.4% (0/15)
MDA	0.1% (0/15)	9.9% (9/15)
Compur	2.7% (1/10)	4.7% (2/10)

*Numbers in parentheses are number of days on which the drift exceeded the 2.5% specification/number of test days.

Table 4. Summary of Calibration Error Tests

	Calibration Error*	
Analyser	Mid-Level (503 ppm)	High-Level (1556 ppm)
Compur Sampling System (40:1 dilution)		
LSI	(+) 3.5%	(+) 37.7%
TECO	(+) 7.9%	(-) 2.3%
MDA	(+) 13.9%	(-) 16.3%
Compur	(+) 7.0%	(+) 10.2%
TECO Sampling System (45:1 dilution)		
LSI+	—	—
TECO	(+) 3.4%	(-) 8.1%
MDA	(+) 8.6%	(-) 21.7%

*The sign within parentheses denotes whether the mean of the monitor responses was greater than (+) or less than (-) the known concentration of the injected calibration gas.
+Not tested on TECO sampling system because of the long response time of the analyser and also the shortage of available calibration gas.

Table 5. Summary of Response Times to HC Gas Injections

System	Response Times (min)
Bodenseewerk Monitoring Systems	3
Compur Monitoring System	5
Compur Sampling System	
LSI	15
TECO	4
MDA	4
TECO Sampling System	
LSI	16
TECO	5
MDA	6

urement system to display 95% of a step change in gas concentration on a data recorder. The response times were determined by injecting zero air and HCl calibration gases through the entire monitoring system. The response times of the LSI, TECO, and MDA analyzers were determined first for samples delivered by the Compur sampling system, and then for samples provided by the TECO sampling system. The results are presented in Table 5.

The results afforded by the various performance tests conducted on both dilution sampling systems indicate no significant difference in the ability of either sampling system to deliver a representative sample to an HCl CEM.

The two primary physical differences between these two similar sampling systems are: (1) the Compur dilution probe sample critical orifice is constructed of stainless steel and is electrically heated to maintain a constant temperature, whereas the TECO dilution probe critical orifice is constructed of glass and is not heated except by the flue gas; and (2) the Compur system delivers diluted sample flow to the CEMs at a rate of approximately 33 L/min, whereas the TECO system delivers sample at approximately 6 L/min.

The dilution ratios of both probes were checked periodically by using a CO analyzer and CO calibration gases. The dilution ratio never changed without indicating a significant change in either the sample orifice vacuum or the dilution air delivery pressure. The dilution ratios were also verified immediately before the initiation of each of the four relative accuracy tests.

The differences noted during three of the four relative accuracy test periods are apparently due to HCl loss in th sampling system. Both sampling system transport the diluted flue gas sample ; relatively high flow rates through hea traced tubing (300ºF). So-called memor effects" (HCl losses due to wall adsor tion of HCl) are less likely to occur und these conditions. The apparent differenc between the duct and manifold sampl results may be attributed to HCl loss t the stainless-steel components on th manifold, which included a few type 31 stainless-steel fittings and ball valve The sample delivered by either samplin system to the common glass manifol passed through the stainless-steel har ware before it entered the HCl imping train. Therefore, because of the potenti for HCl loss, the use of stainless-ste components was minimized wherev possible.

Conclusions

The following conclusions are based on the results that were obtained from the project.

- Except for the CEA Model TGA-410, the HCl monitoring equipment produced effluent measurements in good agreement with concurrent wet-chemistry measurements for uncontrolled HCl emissions from a municipal waste combustion source.
- The TECO 200 and Compur sampling systems (which employ dilution probes), as well as the Bodenseewerk monitoring system (which uses a non-dilution, heat-traced sampling system) can reliably provide representative effluent samples to the analyzers. The relative accuracy results indicate that the effect of HCl line losses can be minimized by injecting the HCl calibration gases through the entire sampling system when performing the dynamic calibrations.
- For some of the analyzers, the calibration gas injections and the relative accuracy tests do not always provide the same indication of CEM performance.
- The relative accuracy test data do not indicate biases for any of the monitor measurement techniques because of analytical interferences present in the effluent of this municipal boiler.

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