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**Demonstration of Multimetal Continuous Emission Monitors for Real-Time Measurement of Trace Hazardous Metals**

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The U.S. Department of Energy and the U.S. Environmental Protection Agency (EPA) cosponsored a study to evaluate three different multimetal continuous emission monitors (CEMs) currently under development within several U.S. government programs. Seven metals plus a tracer metal were injected, as an aqueous spray, into the secondary combustion chamber of the EPA's rotary kiln incinerator simulator (RKIS). The facility was operated at carefully controlled conditions during the test period. Fly ash from a coal-fired boiler was also injected to simulate the particulate loading expected in a real waste combustion environment, and to challenge the CEMs by providing representative spectral interferants. The CEMs and EPA reference method sampling probes were located in the duct downstream from the secondary combustion chamber. Three different metals concentrations were injected, based on proposed EPA emission limits for waste combustion, to achieve high, medium, and low metals concentrations in the duct. The CEM instruments and participating developers were: Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES), U.S. Naval Air Warfare Center, China Lake, CA; and Laser

Induced Breakdown Spectroscopy (LIBS) (one unit each), Diagnostics Instrumentation and Analytical Laboratory (DIAL), Mississippi State University, Starkville, MS; and Sandia National Laboratories, Livermore, CA. All of the CEMs measured at least some of the metals during all of the tests. This paper discusses the results of the tests.

## INTRODUCTION

The 1991 promulgation of regulations governing the destruction of hazardous wastes in boilers and industrial furnaces (BIFs)<sup>1</sup> limits the emissions of trace metals from waste combustion devices. Compliance with these standards requires that the control of the metals be demonstrated during a trial burn. The facility must also demonstrate that metal emissions during post-trial-burn operations are held within the envelope of operations defined in the trial burn. This post-trial-burn compliance is currently demonstrated by limiting the feed rate of each regulated metal. Limiting the feed rate of the metals requires extensive feed characterization, which is a significant expense to the waste combustion facility. CEMs for metals would be an alternative to feed characterization.

Recently, the U.S. Environmental Protection Agency (EPA) proposed additional rules to govern hazardous waste combustion (HWC) facilities.<sup>2</sup> These revised rules would promulgate new emission standards reflecting the performance of the Maximum Achievable Control Technology (MACT) specified by the Clean Air Act and would establish continuous emission monitors (CEMs) as being preferred for compliance monitoring. Compliance monitoring is a multitiered hierarchy of methodologies. The top tier uses direct monitoring of the pollutant in question by CEM. The second tier uses a CEM as a surrogate for the pollutant in question, along with appropriate additional operating controls to account for limitations of the surrogate. Lacking a CEM, the EPA uses the third tier, which involves setting feedstream limitations and operating parameter limits to ensure compliance. This proposed rule is often referred to as the MACT rule and the proposed standards as the MACT standards.

Under the proposed MACT rule, CEMs for hydrogen chloride (HCl), chlorine (Cl<sub>2</sub>), mercury (Hg), semi-volatile metals (SVMs), and low-volatile metals (LVMs) can replace feedstream analysis for those constituents. This is especially important when dealing with mixed waste, for which worker and public exposure must be kept "as low as reasonably achievable," or ALARA.<sup>3</sup>

Given these incentives, government agencies have invested significant funding to develop CEMs capable of monitoring trace levels of toxic metals in flue gases. Multimetal CEMs that satisfy the Performance Specification (PS) in the proposed MACT rule<sup>4</sup> are not yet commercially available; however, several prototype instruments have been developed and tested in the laboratory.

The objective of this project was to test the available prototype multimetal CEMs in a field environment and to determine their relative accuracy (RA) as defined in the EPA PS for multimetal CEMs. Testing was jointly sponsored by U.S. Department of Energy (DOE) and EPA. A committee consisting of members of the sponsoring organizations prepared the test plan and coordinated the testing activities. These tests built upon previous DOE/EPA testing of metal and organic compound CEMs conducted in August 1995 at the EPA Incineration Research Facility (IRF) in Jefferson, Arkansas<sup>5</sup>.

## **EXPERIMENTAL**

Three different multimetal CEM developers participated in the test. Information on each of the CEMs that were evaluated is shown in Table 1. Two of the CEMs (the DIAL/LIBS and Sandia/LIBS) were *in-situ* analyzers, and the third (the Navy/ICP) instrument utilized an isokinetically extractive sample. The developers of the CEMs were responsible for operation and maintenance of their instruments throughout the tests. A data report on the measurements from the CEMs was due to the organizing committee each day during the tests.

The tests were conducted using a simulated flue gas stream produced by the EPA's rotary kiln incinerator simulator (RKIS) facility at the EPA's Environmental Research Center in Research Triangle Park, NC. The RKIS facility consists of a primary combustion chamber, a transition section, and a secondary combustion chamber (SCC). Both the primary burner and SCC are fired with 73 kW (250,000 Btu/hr) natural-gas-fired burners. The RKIS facility and the sampling locations for the CEMs are shown in Figure 1.

Combustion gases exiting the SCC were cooled rapidly to approximately 538 °C (1000 °F) as they passed through a water-jacketed section of ductwork immediately downstream of the SCC. Since the Navy/ICP instrument used Teflon parts in its sample extraction system, it was critical to reduce the flue gas temperature below 260 °C (500 °F) upstream of the Navy/ICP sample probe. Therefore dilution air was added to further cool the gases to 232 °C (450 °F).

Metals were introduced into the system by atomizing 50 mL/min of aqueous solutions of various concentrations of metals into the SCC afterburner. The solution was atomized at the exit of an annulus inside the afterburner's natural gas fuel feed tube, introducing metal-containing aerosol droplets directly into the burner flame.

To ensure a controlled but realistic flue gas environment, a K-Tron screw feeder was employed to inject coal flyash into the transition section as the gases left the kiln section. The addition of flyash provided additional analyte elements (e.g., iron, aluminum, silicon) that can potentially

interfere with spectrometric determination of the target metal analytes. Approximately 1 g/min of flyash was introduced to simulate particulate loading rates similar to those found downstream of electrostatic precipitators (approximately 35 mg/m<sup>3</sup>).

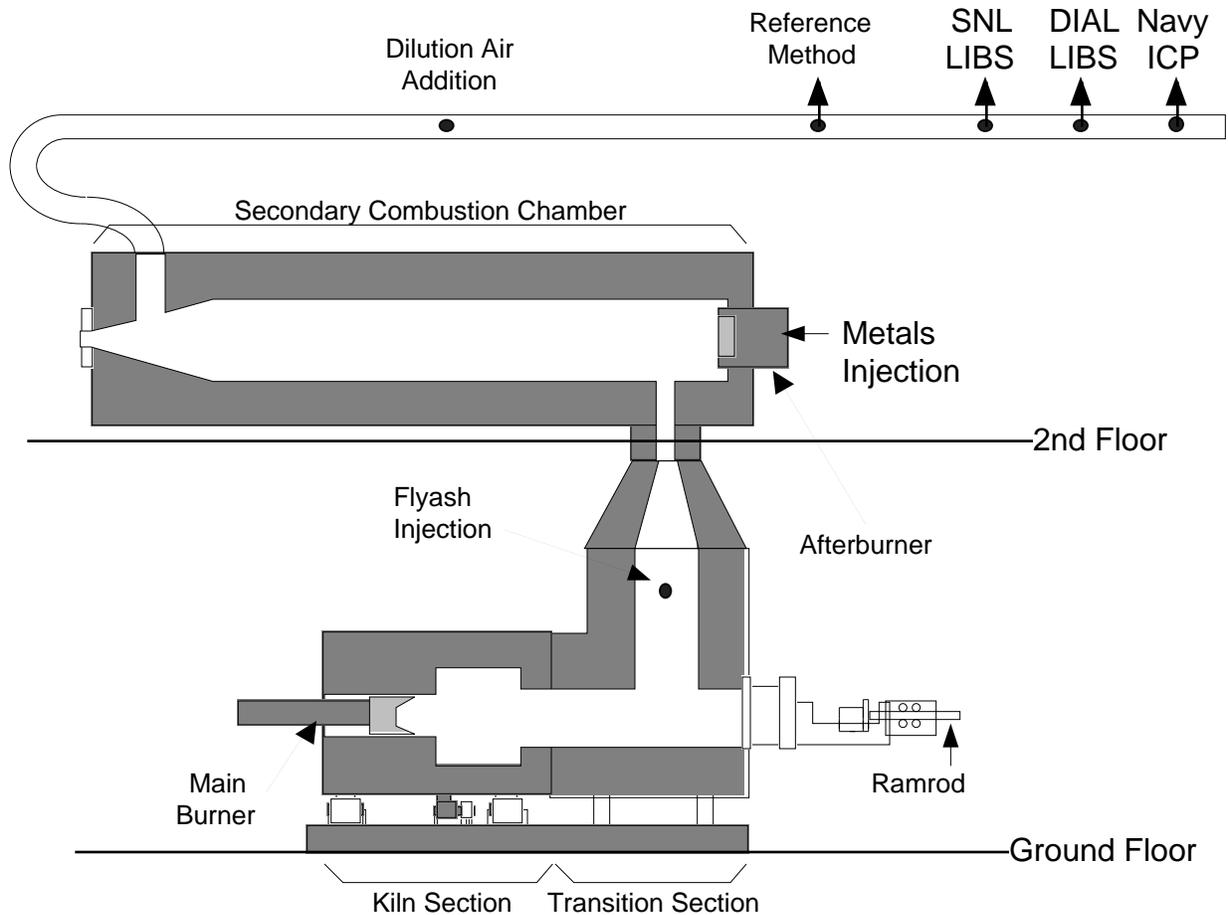


Figure 1. Rotary Kiln Incinerator Simulator

Target flue gas metal concentrations are shown in Table 2. All of the metals noted, except yttrium, are addressed in the proposed MACT rule for HWCs. Yttrium was included at a relatively high, fixed concentration in the feed solution so the developers could use this element as an internal reference, and an indicator of CEM performance.

Each participating CEM had access to one set of sampling ports in the duct. An additional port was used for the EPA Reference Method (RM) sampling, which provided the "true" values of the metals concentrations in the duct to which to compare the CEM measurement results. The EPA RM that was used was EPA Method 0060<sup>6</sup>. Although the PS suggests a minimum of nine repeat RM measurements for a relative accuracy test audit (RATA) test, time did not allow for a complete nine-replicate RATA test to be completed. The number of RM measurements performed for each test concentration depended on the target metal concentration. The RM

sampling time was approximately 2 hours for the low target concentration tests and approximately 1 hour for the medium and high concentration tests. This timing allowed for four RM samples to be collected for the low concentration test day and six RM samples to be collected for the medium and high concentration test days.

At the beginning of each test day, all RM sampling trains were assembled and leak-checked, and the RKIS combustion gas CEMs were calibrated in accordance with facility standard operating procedures. During this time, the metals CEM operators calibrated their instruments and the RKIS system operation was stabilized at the desired operating conditions. After stable RKIS operation was achieved, flyash and metals were injected. CEM developers were given at least 15 minutes notice prior to initiation of RM sampling. Initially, metals injection was started 5 minutes prior to initiation of RM sampling. However, based on feedback from the CEM developers after the first day of testing, this was increased to 15 minutes, since it appeared that metals concentrations took approximately 15-20 minutes to reach constant levels.

## **RESULTS**

Table 3 lists the target concentrations and the respective RM-measured concentrations for each run. The average CEM results for the various RM sampling periods were compared to the corresponding RM results according to the procedure prescribed by EPA for the calculation of the RAs for multimetal CEMs.<sup>3</sup> Note that the RM values for Hg were consistently lower than the target concentrations. It was not known why this anomaly happened. It may be a wall effect where Hg is somehow adhering to the furnace walls. Matrix spikes were performed prior to analyses, and the recovery of the permanganate fraction of those spikes was poor. Because of this, Hg RM results should be viewed with suspicion. The average multimetal CEM results for the RM time periods are shown in Tables 4, 5, and 6 for the DIAL/LIBS, Navy/ICP, and Sandia/LIBS systems, respectively. Note that multiple analyte measurements are reported for the Sandia/LIBS based on multiple spectral wavelengths.

Table 7 summarizes overall performance including the number of target analytes determined by the CEMs at the various test concentrations, QA/QC, and sampling rate information. Only the Navy/ICP was able to determine all of the metals at all of the test conditions. The DIAL/LIBS system required the observation of two to four spectral regions to measure the five analyte metals that were quantified by that instrument during the tests. The RM sampling period was divided among those regions, as the instrument made measurements in one spectral region at a time. The Sandia/LIBS system required the observation of two spectral regions to measure the target metal analytes. Sandia submitted measurements at several wavelengths for Be and Cr. They did not indicate which numbers should be used. Be was measured at a different wavelength at low concentrations.

The LIBS CEMs cannot scan the entire spectral region at one time with a single spectrometer. The technique uses gated detection to reduce background spectral noise, and gated spectrometers capable of scanning the entire spectral region are not yet commercially available. To measure the seven metals in this test, the spectrometers must be physically moved to three different positions. This is borne out in the test results, which show only one to three metals measured at any given time. As a result, each metal was recorded only a fraction of the time during reference method sampling. The DIAL/LIBS system typically recorded data for each metal about 30% of a 1 to 3 hour reference method time interval. However, this varied considerably: as low as 10% and as high as 90% for each metal. Sandia did not report time-specific data, so data acquisition rates could not be calculated, but based on field observations, it would be very low.

The Navy/ICP CEM data acquisition rate is potentially greater than for LIBS because the spectrometer grating is not changed. The ICP sample cycle time for this test was 3.5 minutes, although they state that the system is capable of a 2 minute cycle time. During this cycle time, 6 to 7 seconds of flue gas is introduced. Therefore, the data acquisition rate is 6/210 or 3%. However, the data are spread uniformly over the reference method time, so it is inherently more representative than the LIBS systems. Depending on the characteristic time of transients in flue gas concentrations, the "data acquisition rate" could impact the relative accuracy.

Table 7 also summarizes the average RA results for each CEM under each of the test conditions for all target analytes. One key observation concerning the RAs is that the RA values of 20 % or lower mandated by the performance specification for multimetal CEMs were rarely achieved: the DIAL/LIBS system had none, the Navy/ICP system had three, and the Sandia/LIBS system had one. The average RAs listed in Table 8 showed that none of the CEMs achieved the required 20 % RA. It must be emphasized, however, that to perform a valid RATA test, at least nine CEM/RM measurement pairs must be obtained. The statistical calculation for RA includes a t-test term in the denominator that can dominate the calculation if insufficient measurement pairs have been obtained. For these tests, with at most five measurement pairs, calculated RAs are higher than they would have been had more measurement pairs been taken. It is not clear whether any of the CEMs would have attained the required RAs even if the additional measurements were taken.

## CONCLUSIONS

Three prototype multimetal CEMs were tested in April 1996 at the RKIS at the EPA National Risk Management Research Laboratory, RTP, North Carolina.

The Navy/ICP system provided quantitative CEM results for the seven toxic metals at all three concentration levels. For the seven metals, the Navy/ICP system achieved average relative

accuracies of 74, 66, and 67% for the low, medium, and high concentration levels, respectively. The RA values on individual analytes achieved by the Navy/ICP system ranged between 8 and 143%.

The LIBS systems provided quantitative CEM results for only four toxic metals at the high concentration level, three and two toxic metals, respectively, at the medium concentration level, and only two and one, respectively, at the low concentration level. The DIAL/LIBS system achieved average relative accuracies of 143, 62, and 57% for the low, medium, and high concentration levels, respectively. The DIAL/LIBS RA values ranged from 31 to 273%. The Sandia/LIBS system achieved average relative accuracies of 91, 284, and 524% for the low, medium, and high concentration levels, respectively. The Sandia/LIBS RA values ranged from 5 to 1304%.

Of the three CEMs tested, only the Navy/ICP system provided quantitative results for Hg. The RAs achieved for Hg, however, were not superior to those achieved by the EcoChem Hg-Mat 2 mercury CEM evaluated in the August 1995 performance tests conducted at the EPA IRF.<sup>5</sup> The Navy/ICP system tested there is a multimetal CEM, whereas the EcoChem device is a Hg CEM only.

This test also provides the following information about Minimum Detection Limits (MDLs) of each instrument:

- Both the DIAL and Sandia LIBS systems should have measured Sb at high concentrations (approximately 600 µg/dscm), but did not. Thus, the estimated MDL for Sb needs to be revised for these two systems. Interferences from combustion gases and flyash might cause the MDLs to be higher than originally estimated.
- The DIAL/LIBS system measured Cd at 136 µg/dscm, although its MDL was 240 µg/dscm. The Navy ICP system measured Hg at 1.8 to 3.6 µg/dscm, although its estimated MDL was 5 µg/dscm. Again, the estimated MDL needs to be re-evaluated for each of these cases.
- The Navy/ICP system is far superior in estimated MDL, needing to improve only for Hg to meet target minimum detection limits.
- The DIAL and Sandia LIBS systems need to dramatically improve detection of Pb, Hg, As, and Sb to be useful as a multimetal CEM for hazardous waste effluent monitoring. The target minimum detection limit for these compounds is around 1 µg/dscm. The MDL may be improved by improving the optical and detection systems.

Overall, the test results showed the prototype nature of the test CEMs and the need for further development before multimetal CEMs can succeed in commercial service as envisioned by regulators and citizens. None of the CEMs tested consistently achieved RA values of 20% or

less as required by the performance specification proposed by the EPA in April 1996.<sup>4</sup>  
Instrument size reduction and automation will also be needed for commercialization.

## REFERENCES

- 1 U.S. EPA --Standards for the Management of Specific Hazardous Wastes and Hazardous Waste Management Facilities -Hazardous Waste Burned in Boilers and Industrial Furnaces," in 40 CFR PART 266, Subpart H, U.S. Government Printing Office, Washington, DC, July 1, 1996.
- 2 U.S. EPA Proposed Rule "Hazardous Waste Combustors; Maximum Achievable Control Technologies Performance Standards," in Federal Register, Volume 61, pp. 17357 - 17536, April 19, 1996.
- 3 U.S. Department of Energy "Radiation Protection Programs" in 10 CFR Part 835.101(c), U.S. Government Printing Office, Washington, DC, January 1, 1997.
- 4 U.S. EPA Proposed Rule "Hazardous Waste Combustors; Maximum Achievable Control Technologies Performance Standards (Performance Specifications)," in Federal Register, Volume 61, pp. 17499 - 17502, April 19, 1996.
- 5 Ghorishi, S. B., W. E. Whitworth, Jr., C. G. Goldman, and L. R. Waterland, "Testing the Performance of Real-Time Incinerator Emission Monitors," EPA-600/R-97-024 (NTIS PB97-142871), National Risk Management Research Laboratory, U. S. EPA, Cincinnati, Ohio, March 1997.
- 6 U.S. EPA, "Test Methods for Evaluating Solid Waste: Physical/Chemical Methods," EPA SW-846, Method 0060 "Determination of Metals in Stack Emissions," 3rd edition, Revision 2, September 1994.

Table 1. Multimetal CEM Participants

CEM Name	Principle of Operation	Developer
Laser Induced Breakdown Spectroscopy (LIBS)	The wavelengths and intensities of light emitted by atoms excited by laser pulses depend on the kinds and numbers of atoms present	Diagnostic Instrumentation and Analysis Laboratory (DIAL) at Mississippi State University, Starkville, Mississippi
Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES)	The wavelengths and intensities of light emitted by atoms excited when sample gas is passed through an ICP depend on the kinds and numbers of atoms present	Naval Air Warfare Center, China Lake, California, and Thermal Jarrel Ash
Laser Induced Breakdown Spectroscopy (LIBS)	The wavelengths and intensities of light emitted by atoms excited by laser pulses depend on the kinds and numbers of atoms present	Sandia National Laboratories, Livermore, California

Table 2. Test Metals and Target Flue Gas Concentrations ( $\mu\text{g}/\text{dscm}$ )

Metal	Low	Medium	High
Sb	15	60	600
As	15	60	600
Be	15	60	600
Cd	15	60	600
Cr	15	60	600
Pb	15	60	600
Hg	25	100	1000
Y	100	100	100

Table 3. RM Measured Concentrations and Target Metal Concentrations ( $\mu\text{g}/\text{m}^3$ )

Date	Run		Concentration								
			Sb	As	Be	Cd	Cr	Fe	Pb	Hg	Y
4/22/96	1	M	60.9	71.2	50	54.7	65.7	4203	91.9	60.4	100
4/22/96	2	M	62.4	73.4	61.6	59.5	61	3213	80	68.1	119
4/22/96	3	M	53.4	67.8	55.2	54.4	56.9	2721	74	54.9	110
4/22/96	4	M	49.3	63.7	53.8	51.7	52.3	1759	72.3	77.9	105
4/22/96	5	M	43.4	57.1	47.7	46.1	47.2	2867	69.8	46.2	92.2
	Avg		53.9	66.6	53.7	53.3	56.6	2953	77.6	61.5	105
4/23/96	B	-	4.8	12	2.3	4.2	20.2	2212	12.2	NA	7.6
4/24/96	1	L	15	20.1	14.5	12.6	19	2212	18.7	2.8	115
4/24/96	2	L	14.1	17.4	12.8	10.7	20.1	2737	17.8	1.9	99.8
4/24/96	3	L	15.3	16.2	12.3	9.6	19.8	2279	15.5	1.4	97.2
4/24/96	4	L	10.5	14.4	11	8.5	13.7	1671	14.9	1.4	91.7
	Avg		13.7	17	12.7	10.4	18.2	2225	16.7	1.9	101
4/25/96	1	M	56	47.4	52.1	45.5	33	2269	51.1	6.2	110
4/25/96	2	M	63.2	54.8	52.6	46	38.1	2389	57.7	5.8	114
4/25/96	3	M	61.3	50.2	51.6	43.8	35	2178	52.2	7.4	112
	Avg		60.2	50.8	52.1	45.1	35.4	2279	53.7	6.5	112
4/26/96	1	H	269	334	272	356	176	2311	375	311	59.7
4/26/96	2	H	376	396	474	447	180	2698	458	251	90.8
4/26/96	3	H	337	338	436	377	153	1935	375	420	89
4/26/96	4	H	413	402	509	441	169	1542	446	423	95.4
4/26/96	5	H	433	460	549	500	216	2327	489	222	93.4
	Avg		366	386	448	424	179	2163	429	325	85.7

B - blank with only flyash

L - low target concentration

M - medium target concentration

H - high target concentration

Table 4. DIAL/LIBS CEM Results ( $\mu\text{g}/\text{m}^3$ )

Date	Run	Be	Cd	Cr	Pb	Y
4/22/96	1	38.2		69.7		66.9
4/22/96	2	39		43.7		27.3
4/22/96	3	41.9		31		24.4
4/22/96	4	40.3		29.3		85
4/22/96	5	32.8		30.9		68.8
	RA	38%		53%		89%
4/24/96	1	29.2		22.6		202.6
4/24/96	2	20.1		17		133.4
4/24/96	3	33		16.8		108.3
4/24/96	4	42.3		15.4		96.1
	RA	273%		31%		93%
4/25/96	1	73.8	55.8	17.5		108.6
4/25/96	2	65.7	52.4	27.7		100.5
4/25/96	3	45.5		18.5		55.4
	RA	86%	73%	61%		86%
4/26/96	1	103		197	275	
4/26/96	2	490	631	276	536	
4/26/96	3	526	554	299	608	
4/26/96	4			236	488	
4/26/96	5	398	534	272	540	
	RA	57%	77%	76%	49%	

Table 5. Navy-TJA/ICP-AES CEM Results ( $\mu\text{g}/\text{m}^3$ )

Date	Run	As	Be	Cd	Cr	Hg	Pb	Sb	Y
4/22/96	1	44.4	29.2	32.5	26.4	8.2	35.5	38.8	57.6
4/22/96	2	44.9	26.1	25.5	12.9	3.7	22.6	37.4	53.8
4/22/96	3	36.1	23.1	24	15.1	2.8	26.3	31.1	48.7
4/22/96	4	51.5	29.8	28.7	13.5	4.1	23.8	39.3	55.8
4/22/96	5	52.4	20.8	20.3	13.5	2.3	18.5	33.7	40.1
RA		53%	66%	63%	83%	117%	74%	50%	62%
4/24/96	1	14.5	9.4	7	6.5	1.3	5.4	23.5	73.7
4/24/96	2	21.7	9.7	7	6.4	1.1	5.6	19.2	77
4/24/96	3	25.6	10.7	8	7.4	1.1	6.8	20.9	86.1
4/24/96	4	23.2	8.9	6.6	6.5	0.9	5.6	17	79.3
RA		90%	43%	59%	88%	86%	86%	64%	44%
4/25/96	1	65.7	52.5	42.4	12	8.3	23.9	65.1	75.1
4/25/96	2	66.9	52.2	41.9	11.4	6.8	22.2	61.7	77.3
4/25/96	3	24.6	49.2	38.3	10.4	5.6	18.9	65.3	75.2
RA		119%	8%	16%	88%	86%	79%	28%	35%
4/26/96	1	NM							
4/26/96	2	294	385	295	71.8	23.9	154	373	53
4/26/96	3	305	383	262	58.4	26.9	140	345	50
4/26/96	4	331	439	301	65.3	28.5	164	419	57
4/26/96	5	298	399	278	51.9	26.4	125	373	52
RA		45%	32%	52%	93%	143%	86%	16%	45%
NM - not measured									

Table 6. SNL/LIBS CEM Results ( $\mu\text{g}/\text{m}^3$ )

Analyte/ Wave- length	Be/265.1	Be/265.1	Be/313.1	Be/313.1	Be/313.1	Cd/226.5	Cr/267.7	Cr/283.6	Cr/283.6	Pb/220.4	
Date	Run										
4/22/96	3	68.8	22.5			69.8	182.2				
4/22/96	4	46.2	25		50.8	44.6	97.7				
4/22/96	5	32.4	14.9		23.3	38.2	58.4				
RA		77%	66%		296%	68%	413%				
4/24/96	1					24.9					
4/24/96	2					23.5					
4/24/96	3					20.4					
4/24/96	4					19.4					
RA						91%					
4/25/96	1					54.5	182.9				
4/25/96	2					55	160.7				
4/25/96	3										
RA						5%	591%				
4/26/96	1	386.3	72.4	380.6	465.6		866.3	182.8	233.7	389.6	2235
4/26/96	2		64				583.4	180.4	215		1514
4/26/96	3		49.2	276.3			478				1361
4/26/96	4		51.8	265.6	243.4		355.6	124.2	108.2	125.9	1135
4/26/96	5	167.6	40.4	214.3	197.2		342.1	807.4	95.2	3943.8	1131
RA		800%	120%	105%	196%		100%	335%	84%	3494%	386%

Table 7. Overall Performance of Multimetal CEMs

Technology Developer	Average Relative Accuracy for Some or All Metals at Concentrations			QA/QC Performed	Sample Frequency	Time to Analyze Data
	High $\approx$ 600 $\mu\text{g}/\text{m}^3$	Medium $\approx$ 60 $\mu\text{g}/\text{m}^3$	Low $\approx$ 15 $\mu\text{g}/\text{m}^3$			
Navy/ICP	67% for all 7 metals	72% for all 7 metals	74% for all 7 metals	Daily calibration & zero check. None failed during test week. Reprofiled spectrometer every 30 minutes.	One 6 to 7 second sample taken every 3 to 4 minutes.	Four minutes
DIAL/LIBS	65% for 4 of 7 metals	55% for 3 of 7 metals	152% for 2 of 7 metals	Daily zero check – record spectra w/no metal or ash running. Adjusted background on Day 5 of testing based on zero check.	5 samples per second, averaged over 100 samples. 3 spectrometer grating positions moved every 5 minutes.	Seconds to analyze data. Minutes to move spectrometer
Sandia/LIBS	173% for 4 of 7 metals	240% for 2 of 7 metals	n/a	Single-time calibration check using portable aerosol generator outside the stack. Spectral calibration using mercury discharge lamp several times daily. Zero check once early in test week.	4 samples per second, averaged over 100 samples. 3 spectrometer grating positions moved every 5 minutes.	Minutes to analyze data. Minutes to move spectrometer