

PERFORMANCE TESTING OF MULTI-METAL CONTINUOUS EMISSIONS MONITORS

Appendix Volume 1

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The testing described in this report adds to the information and experience gained during previous DOE/EPA testing of metal and organic compound CEMs conducted in August 1995 at the EPA Incineration Research Facility (IRF) in Jefferson, Arkansas. The success of this testing owes much to many of the same persons who planned and carried out the IRF test program.

Most importantly, all the persons named in this report, and others, from high organizational levels and principal investigators to workers, deserve real praise for the exemplary degree to which each contributed to this multi-organizational and multi-disciplinary team achievement.

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FINAL REPORT OF DIAL CEM DEVELOPER TEAM

**DOE AND EPA CONTINUOUS EMISSION
MONITORING TEST AT EPA NATIONAL RISK
MANAGEMENT RESEARCH LABORATORY
(NRMRL)**

**Research Triangle Park
Raleigh, North Carolina
April 22 - 26, 1996**

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RKIS LIBS MEASUREMENT

Laser-induced breakdown spectroscopy (LIBS) is a laser-based diagnostic technique for measuring the concentration of toxic metals in the offgas emission from various waste treatment facilities. DIAL's LIBS system for offgas emission monitoring has been successfully demonstrated at the Western Environmental Technology Office (WETO)/MSE. It has also been successfully used to monitor various toxic metals in the offgas emission of a PT-150 Plasma Energy Corporation plasma torch during test runs of the Savannah River simulated test feed at DIAL/MSU. The LIBS system has also been demonstrated as a real time metal emission monitor during tests at the STAR Center (June 1995) and Westinghouse Savannah River Company (WSRC) (February 1996).

Description

The principle of the LIBS technique is illustrated in Figure 1. A pulsed laser beam is focused at the test point and produces a spark due to the high electric field. The spark generates a high density plasma which excites various atomic elements present in the focal volume. The atomic emission from the plasma is collected with a collimating lens and sent to the detection system. The intensity of the atomic emission lines observed in the LIBS spectrum are then used to infer the concentration of the atomic species.

Figure 2 shows the experimental setup of DIAL's LIBS system. A frequency doubled Nd:YAG laser beam is focused at the probed volume through an optical port. The port is purged with nitrogen to keep the window clean and cool. The same port is used to collect the LIBS signal. A beam dump mounted on the opposite port across the gas stream is used to dump the laser energy. A third port normal to the laser beam is used to monitor the spark in the gas stream and also to align the spark with the sample injection probe for calibration. The emission from the spark is collected with a UV optical fiber bundle coupled to a spectrograph. An intensified diode array detector (IDAD) is attached to the spectrograph to record the LIBS spectrum. A laptop computer interfaced to the detector controller with a PCMCIA-GPIB card is used for data acquisition/analysis.

The DIAL/LIBS system is mobile and versatile. It weighs approximately 220 lb. The instrument requires a space of 42 in. x 24 in. x 30 in. near the optical port. The laser power supply occupies a space of 21 in. x 11 in. x 20 in. which can be kept ~ 13 ft from the laser head. A 110-V, 10-A line for the LIBS detection system and a 220-V, 10-A, single-phase line for the laser power sup-

ply are required for operating the LIBS system. A cylinder of ultra-high purity N_2 is needed to purge the detector system. Tap water is also required to cool the detector and the LIBS probe. A cylinder of compressed air is used while performing calibration with an ultrasonic nebulizer.

Standard Operating Procedure

The DIAL/LIBS system provides near real time monitoring of the toxic metal concentrations. The spectra of preselected spectral regions is first recorded in the test medium. To obtain good spectral resolution, a 2400-line/mm grating is used in most of the metal measurements. A 1200-line/mm grating is used to simultaneously monitor Pb and Cr during the high metal concentration test. The spectral regions which give the strongest emission lines with minimum interference from other lines are selected for metal CEM testing. The sample, or data rate, depends on the concentration of the toxic metals in the off-gas emission. To obtain a good signal-to-noise ratio, the typical sample time is 26 seconds which corresponds to an average of 260 laser pulses. The intensity of the atomic emission lines observed in the LIBS spectrum are used to infer the concentration of the atomic species using the calibration data obtained from a nebulizer. A user developed macro program running under the EG&G OMA2000 software is used to collect, analyze and display LIBS data in near real time. Figure 3 shows the computer display during the LIBS data acquisition. Each day, LIBS spectra are recorded before the metal injection for zero check.

Calibration

The DIAL/LIBS system was calibrated for all RCRA metals with an ultrasonic nebulizer system at the DIAL laboratory. The calibration is based on the peak height and peak area of each selected analyte line. The peak area, or peak height, of the analyte lines from the test LIBS spectra are normalized with the calibration factor to obtain the metal concentrations. In general, peak height calibration and peak area calibration give about the same result for the interference-free line. For different types of spectral interferences, either peak height or peak area must be selected for best results. The on-site calibration for Cr was performed at the RKIS after the shakedown test on April 19, 1996. Calibrations were also performed every day after the test run with Cr to verify the system response. Since no Cd 228.8 nm calibration was made before the test run, on-site calibrations for Cd 228.8 nm line were also made on April 25 and April 26 and scaled with the Cr calibration to be used to infer the Cd concen-

tration from these two tests. Calibration of the Be 234.8 nm line was also made on April 26 to compare with the calibration of the Be 313.3 nm line.

Performance Claims

The detection limits of the selected analyte lines of ten RCRA metals are listed in Table 1. The detection limits were determined from the LIBS calibration data obtained with an ultrasonic nebulizer. The precision and accuracy of these measurements were estimated from the calibration data and are also listed in Table 1. The precision and accuracy greatly depends on the laser pulse-to-pulse fluctuation and the concentration variation in the metal flow from an ultrasonic nebulizer. The accuracy and precision of LIBS measurements can be improved by increasing the signal integration time. Since some line interferences, such as Ti 326.16 nm next to Cd 326.15 nm and Fe 259.8 nm next to Sb 259.81 nm, were found in the presence of fly ash in the gas stream, the actual detection limits may be slightly higher than the claimed values depending on the concentration of the interfering elements. An alternate line at 228.8 nm for Cd was selected for later measurements. It should be noted that the detection limits of the RCRA metals listed in Table 1 can be reduced by improving the optical design and detection system in the future.

Results and Discussion

The concentrations of Be and Cr were successfully measured in all the tests. The concentration of Cd was measured in the medium and high metal test. The Pb concentration was measured in the high concentration test. A detailed description of the observations and maintenance activities during the test is given in Appendices A - D. The results of each test day are summarized below.

On the first test day (April 22), we monitored spectral regions of 405, 426, 320 and 260 nm. Each spectral region was monitored for 15 minutes. LIBS data sampling time was 6.7 seconds, which corresponds to an average of 66 laser pulses. Although Pb 405 nm and Cd 326 nm lines were monitored during the test, the results of the analysis of these two metals were not reported due to problems of spectral interference and target concentration near the LIBS detection limit. Attempts to monitor Sb and Hg at the 260-nm spectral region failed due to the target concentration below the LIBS detection limit. Concentrations of Cr, Y and Be were successfully measured during the test. Figure 4 shows the variation of metal concentrations during this test. The metal concentrations measured are listed in Table 2. It should be noted that there is a long response

time between metal injection and a steady state condition (see Figure 4). Thus, the data collected in this test probably is not appropriate for direct comparison with EPA Method 29.

On the second test day (April 24), Cr, Be and Y were monitored from two spectral regions. Each spectral region was monitored for ~20 to 40 minutes during EPA sampling. LIBS data sampling time was initially set to 12 seconds and increased to 26 seconds (equivalent to an average of 260 laser pulse) after 9:59 AM to achieve better signal-to-noise data. The error due to laser shot-to-shot fluctuation and random noise is expected to be reduced by longer signal integration time. A plot of time versus measured Be, Cr and Y concentrations is shown in Figure 5. It is clear from the figure that the Be concentration gradually increased to a steady state in the first half hour of the test after the metal injection started. The real time plot also shows the metal concentration quickly drops to zero when the metal injection is turned off. The level of the metal concentrations was found to be more stable in the later part of the test when metal injection was continuous. The time averaged results of this test are shown in Table 3.

On April 25, the medium concentration metal test was repeated. Cd, Be, Cr and Y were monitored from the 230, 313 and 426-nm spectral regions during this test. A Cd line in the 320-nm spectral region, which was monitored on the first test day, has a strong spectral interference. To obtain Cd concentrations, the 230-nm spectral region was selected to be monitored in this test. The Be line at 234.8 nm and Cd line at 228.8 nm were simultaneously monitored in the 230-nm spectral region. The sampling time was kept to 26 seconds in this test. The real time data of this test is shown in Figure 6. The time averaged results of this test are summarized in Table 4.

On the last test day (April 26), Cr and Pb were monitored simultaneously in the 420-nm spectral region with a 1200-line/mm grating, and Cd and Be were monitored simultaneously in the 230-nm spectral region with a 2400-line/mm grating. Hg and Sb were not monitored in this test because the spectra recorded on April 25 at high metal concentrations did not show visible signals from these two elements. Typical spectra from the 230-nm and from the 420-nm spectral regions are shown in Figures 7 and 8. The initial data starting around 8:30 AM indicated that there was little ash in the gas stream and the metal levels were below specifications (see Appendix D). This facility problem was cleared up around 10 AM. In general, each selected spectral region was monitored for ~ 15 to 30 minutes during EPA sampling. However, only Cr and Pb were monitored during RM #4 due to a fire alarm. At the end

of the run, it was found that the laser optics harmonic separator mirror was seriously damaged, and the lens was dirty. The intensity of the emission light was only roughly corrected for signal attenuation due to the dirty window using the background signal as a reference. The damaged laser optics reduced the laser power at the focal volume and produced a weaker laser spark. The effect of the weaker spark might be different for different analyte lines which were not corrected for the measurement. This might have degraded the accuracy of the measurement. A subroutine will be added to the LIBS program to automatically correct in real time the calibration factor for the changes in the window transmission, laser power and other gas stream conditions. The real time LIBS results from this test are shown in Figure 9, and the summary of the test results is shown in Table 5.

Conclusions

The LIBS system was successfully used to monitor concentrations of the selected toxic metals in near real time. The concentrations of Be and Cr were measured in all the tested metal levels. The concentration of Cd was measured in medium and high metal feed tests. The Pb concentration was only measured at the high concentration. Although, the present LIBS system can only be used as a CEM to monitor concentrations of Be, Cr and Cd, its capability to provide instant indication of systems problems has been well demonstrated in this test. Further work on improving the detection limits of Pb, Hg, As and Sb will continue for detection in the low concentration level.

Table 1: DIAL/LIBS minimum detectable concentration limits for the selected metals.

Element	Analyte Line (nm)	Minimum Detectability (μ g/acm)	Relative Precision (%)	Relative Accuracy (%)
As	278.02	600	25	9
Be	234.8	1	12	3
Cd	326.11	120	18	3
Cr	425.44	6	10	15
Co	345.35	24	20	8
Hg	253.65	680	8	13
Mn	257.61	4	18	4
Ni	341.48	30	3	9
Pb	405.78	68	8	13
Sb	259.81	120	20	9
Be	313.04	< 0.1	13	6
Cd	228.8	39	12	9

Table 2: Metal concentration measurements on April 22, 1996.

Time	Time Averaged Concentration (μ g/acm)		
	Cr	Be	Y
09:02 - 09:12	35 \pm 11		34 \pm 21
09:28 - 09:31		13 \pm 4	
10:10 - 10:17		23 \pm 4	
RM#1 Average	35 \pm 11	19 \pm 6	34 \pm 21
11:05 - 11:19	22 \pm 5		14 \pm 10
12:10 - 12:18		20 \pm 7	
RM#2 Average	22 \pm 5	20 \pm 7	14 \pm 10
13:17 - 13:27	16 \pm 5		12 \pm 8
13:28 - 13:33		21 \pm 4	
RM#3 Average	16 \pm 5	21 \pm 4	12 \pm 8
16:15 - 16:21		21 \pm 3	
16:22 - 16:32	15 \pm 4		34 \pm 16
RM#4 Average	15 \pm 4	21 \pm 3	34 \pm 16
17:06 - 17:17	18 \pm 5		43 \pm 22
17:28 - 17:37		20 \pm 10	
18:03 - 18:09		8 \pm 2	
18:20 - 18:30	13 \pm 3		25 \pm 15
RM#5 Average	16 \pm 5	15 \pm 10	35 \pm 21

Table 3: Metal concentration measurements on April 24, 1996.

Time	Time Averaged Concentration (μ g/acm)		
	Be	Cr	Y
08:55 - 09:09	9 \pm 1		
09:11 - 09:24		11 \pm 2	79 \pm 33
09:26 - 09:39	18 \pm 2		
09:42 - 09:55		15 \pm 3	178 \pm 65
10:21 - 10:35		10 \pm 5	65 \pm 11
10:37 - 11:06	18 \pm 2		
11:09 - 11:21		10 \pm 2	96 \pm 29
RM#1 Average	15 \pm 4	12 \pm 4	104 \pm 60
11:41 - 12:04	6 \pm 2		
12:06 - 12:35		9 \pm 3	75 \pm 32
13:00 - 13:08	13 \pm 2		
13:12 - 13:41		9 \pm 1	64 \pm 16
13:43 - 14:00	12 \pm 3		
RM#2 Average	10 \pm 5	9 \pm 2	70 \pm 26
14:40 - 15:33	14 \pm 1		
15:34 - 15:40		11 \pm 2	62 \pm 14
16:03 - 16:39		8 \pm 3	54 \pm 16
16:41 - 17:03	24 \pm 4		
RM#3 Average	17 \pm 5	9 \pm 3	56 \pm 16
17:35 - 18:10	23 \pm 3		
18:12 - 18:35		8 \pm 2	50 \pm 11
19:05 - 19:41		8 \pm 2	49 \pm 13
19:42 - 20:05	20 \pm 3		
RM#4 Average	22 \pm 3	8 \pm 2	49 \pm 12

Table 5: Metal concentration measurements on April 26, 1996.

Time	Time Averaged Concentration (μ g/acm)			
	Cr	Pb	Cd	Be
10:20 - 10:28				99 \pm 4
10:28 - 10:50			322 \pm 34	286 \pm 21
11:10 - 11:38	140 \pm 12	273 \pm 34		
RM#2 Average	140 \pm 12	273 \pm 34	322 \pm 34	228 \pm 89
12:02 - 12:14	151 \pm 20	307 \pm 37		
12:16 - 12:32	291 \pm 53			236 \pm 43
12:50 - 13:20			276 \pm 26	252 \pm 15
RM#3 Average	151 \pm 20	307 \pm 37	281 \pm 38	246 \pm 29
13:49 - 14:15	122 \pm 18	253 \pm 42		
14:30 - 15:00	118 \pm 20	242 \pm 33		
RM#4 Average	120 \pm 19	247 \pm 38		
15:30 - 15:58			268 \pm 43	185 \pm 28
15:59 - 16:28	136 \pm 24	272 \pm 43		
RM#5 Average	136 \pm 24	272 \pm 43	268 \pm 43	185 \pm 28

Table 4: Metal concentration measurements on April 25, 1996.

Time	Time Averaged Concentration (μ g/acm)			
	Be	Cr	Y	Cd
10:36 - 10:51		9 \pm 2	57 \pm 14	
10:51 - 11:06	33 \pm 2			
10:10 - 10:17	69 \pm 22			68 \pm 29
RM#1 Average	49 \pm 23	9 \pm 2	57 \pm 14	68 \pm 29
11:43 - 11:58		14 \pm 2	55 \pm 17	
11:59 - 12:13	27 \pm 2			
12:14 - 12:29	61 \pm 8			100 \pm 15
RM#2 Average	44 \pm 18	14 \pm 2	55 \pm 17	100 \pm 15
13:22 - 13:40	23 \pm 1			
13:41 - 13:55	44 \pm 5			80 \pm 14
14:08 - 14:23		10 \pm 1	28 \pm 10	
RM#3 Average	32 \pm 11	10 \pm 1	28 \pm 10	80 \pm 14

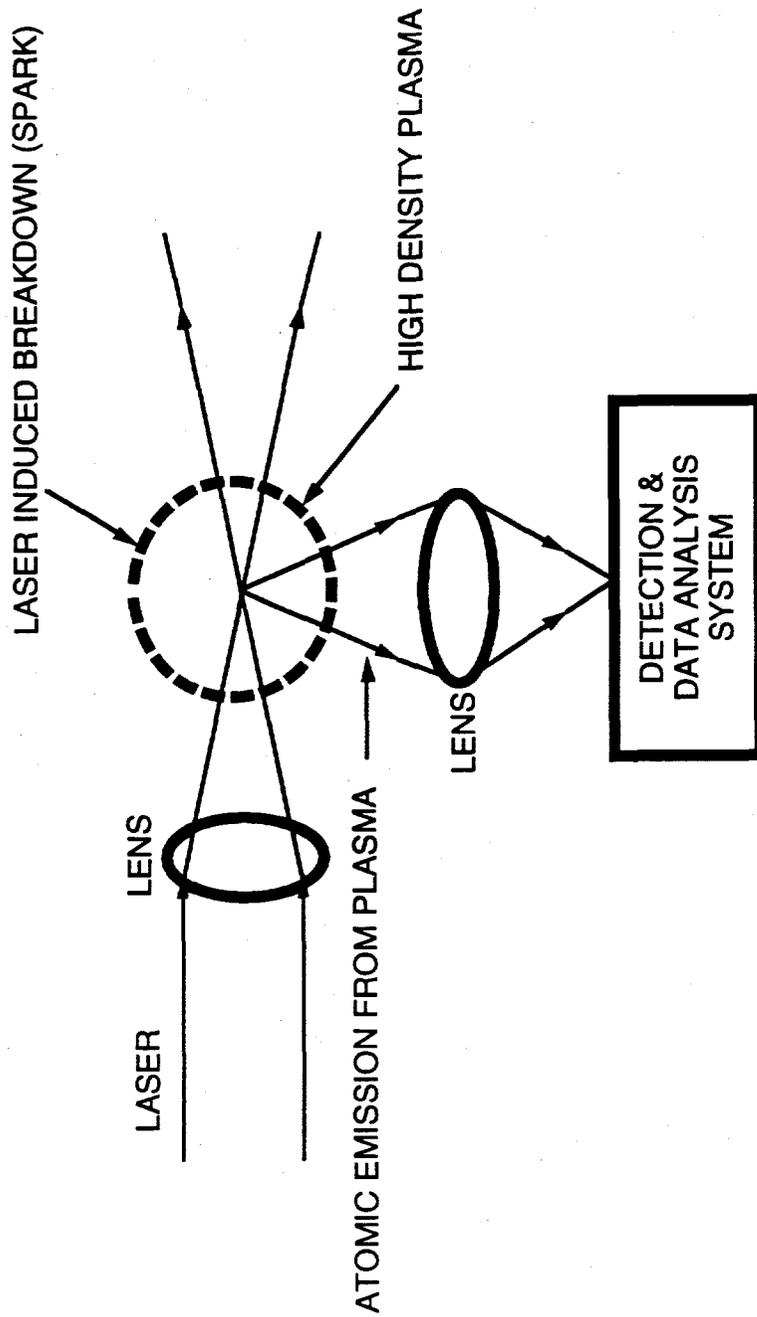
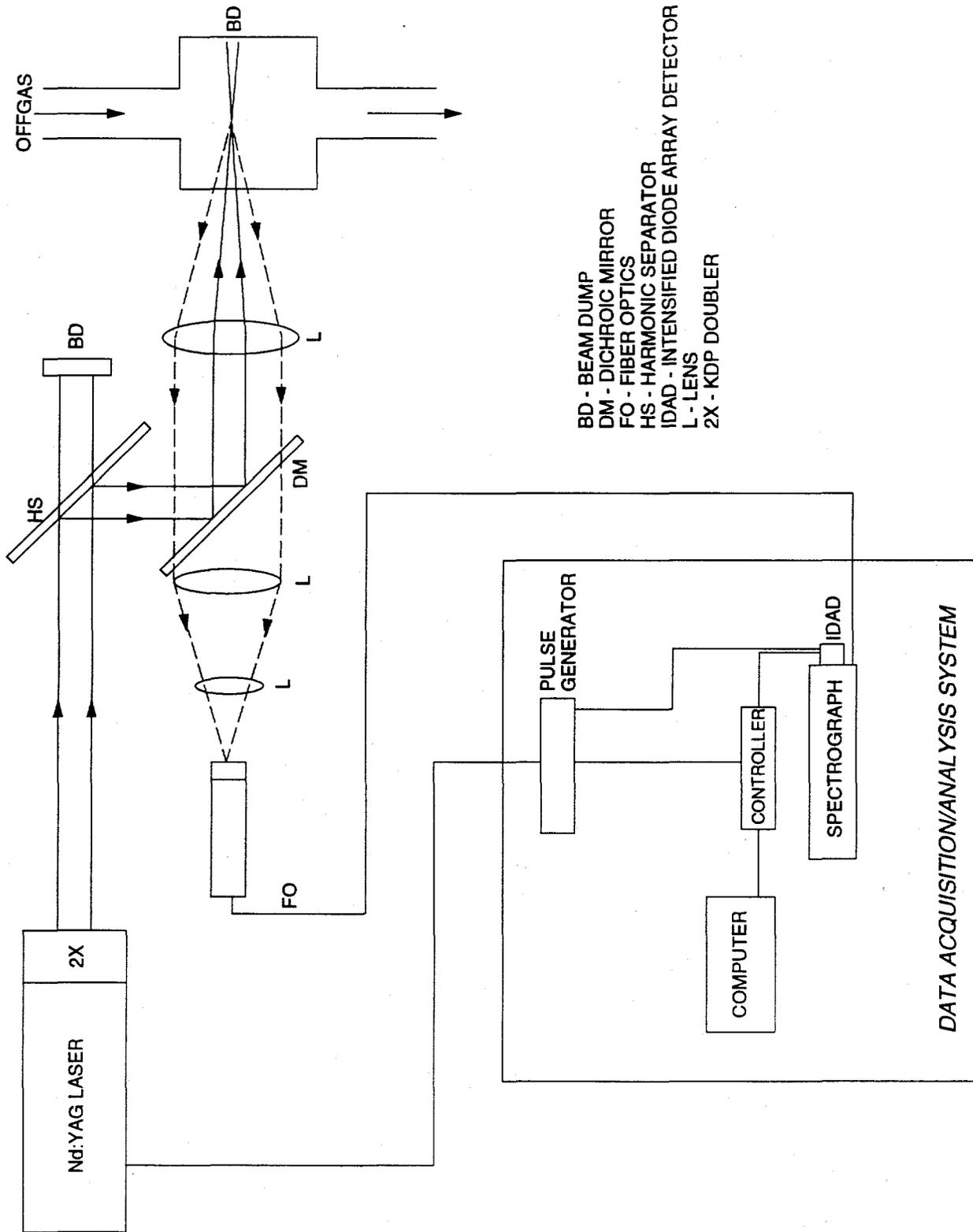


Figure 1
Principle of laser-induced breakdown spectroscopy.



BD - BEAM DUMP
 DM - DICHRIC MIRROR
 FO - FIBER OPTICS
 HS - HARMONIC SEPARATOR
 IDAD - INTENSIFIED DIODE ARRAY DETECTOR
 L - LENS
 2X - KDP DOUBLER

Figure 2
 Experimental setup of laser-induced breakdown spectroscopy system.

FIGURE 2 - DIAL MSU

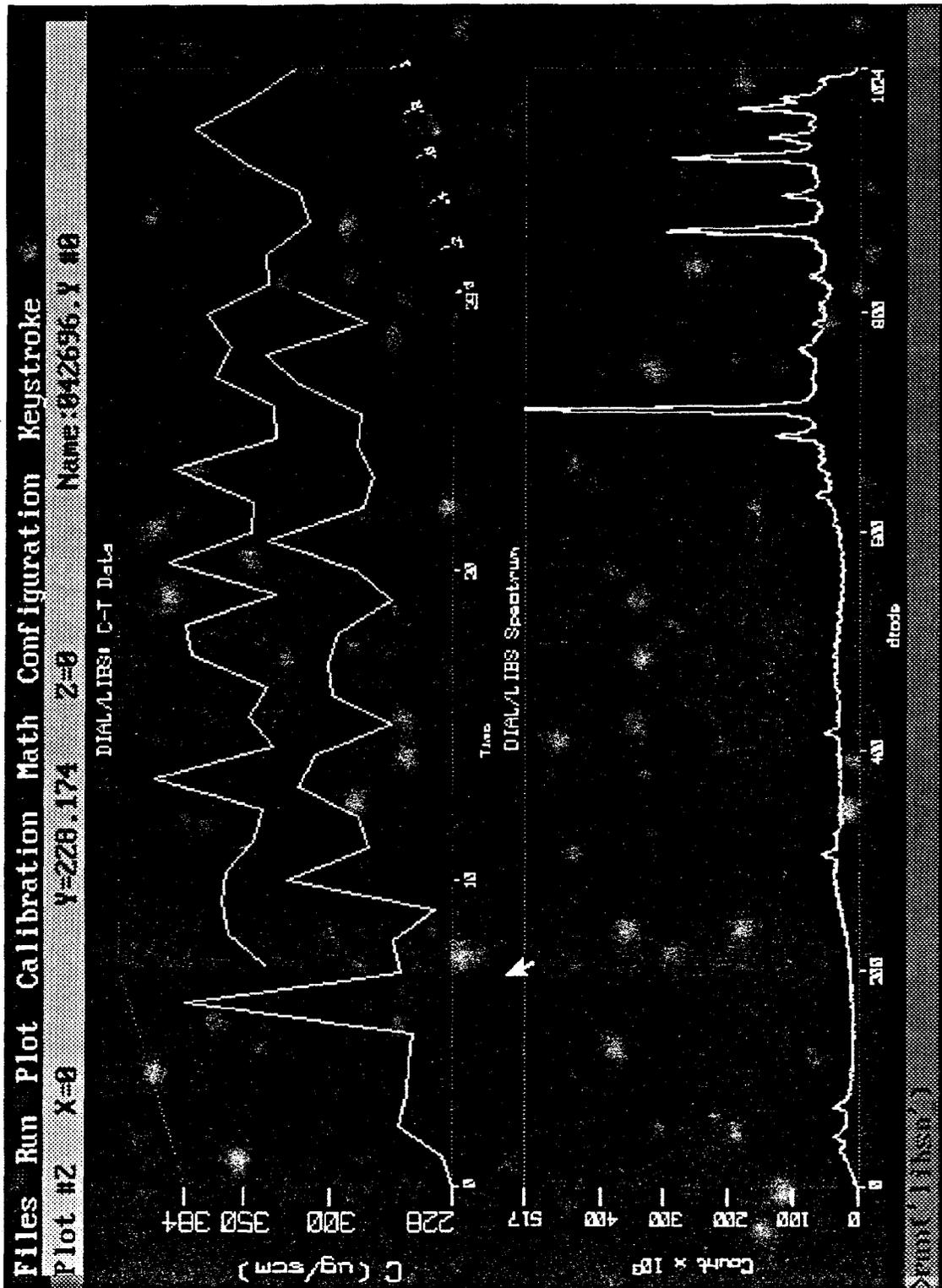


Figure 3
 Computer display during the LIBS data acquisition.

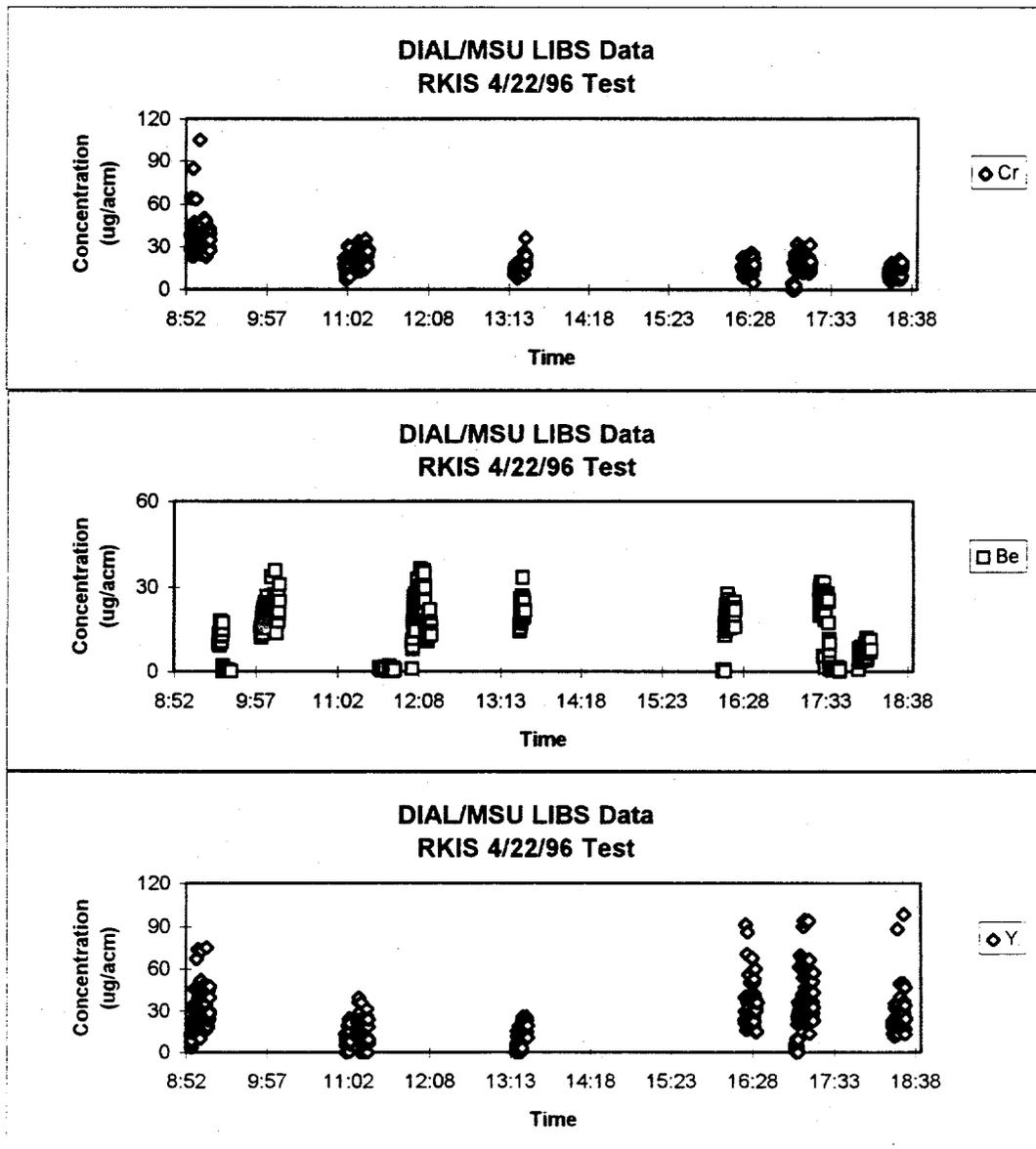


Figure 4
Concentration of Be, Cr and Y at different times during April 22, 1996 test.

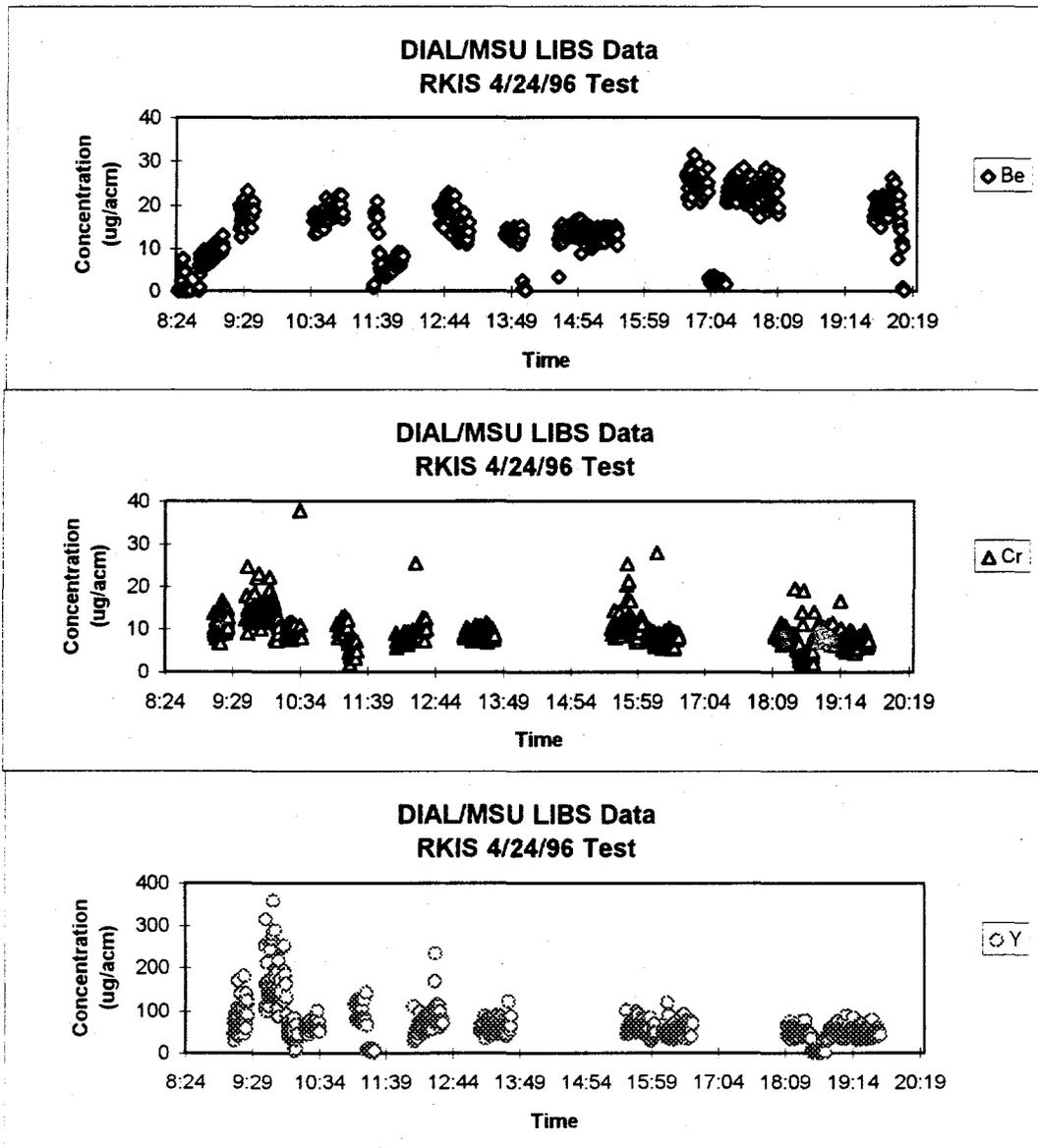


Figure 5
Concentration of Cr, Be and Y at different times during April 24, 1996 test.

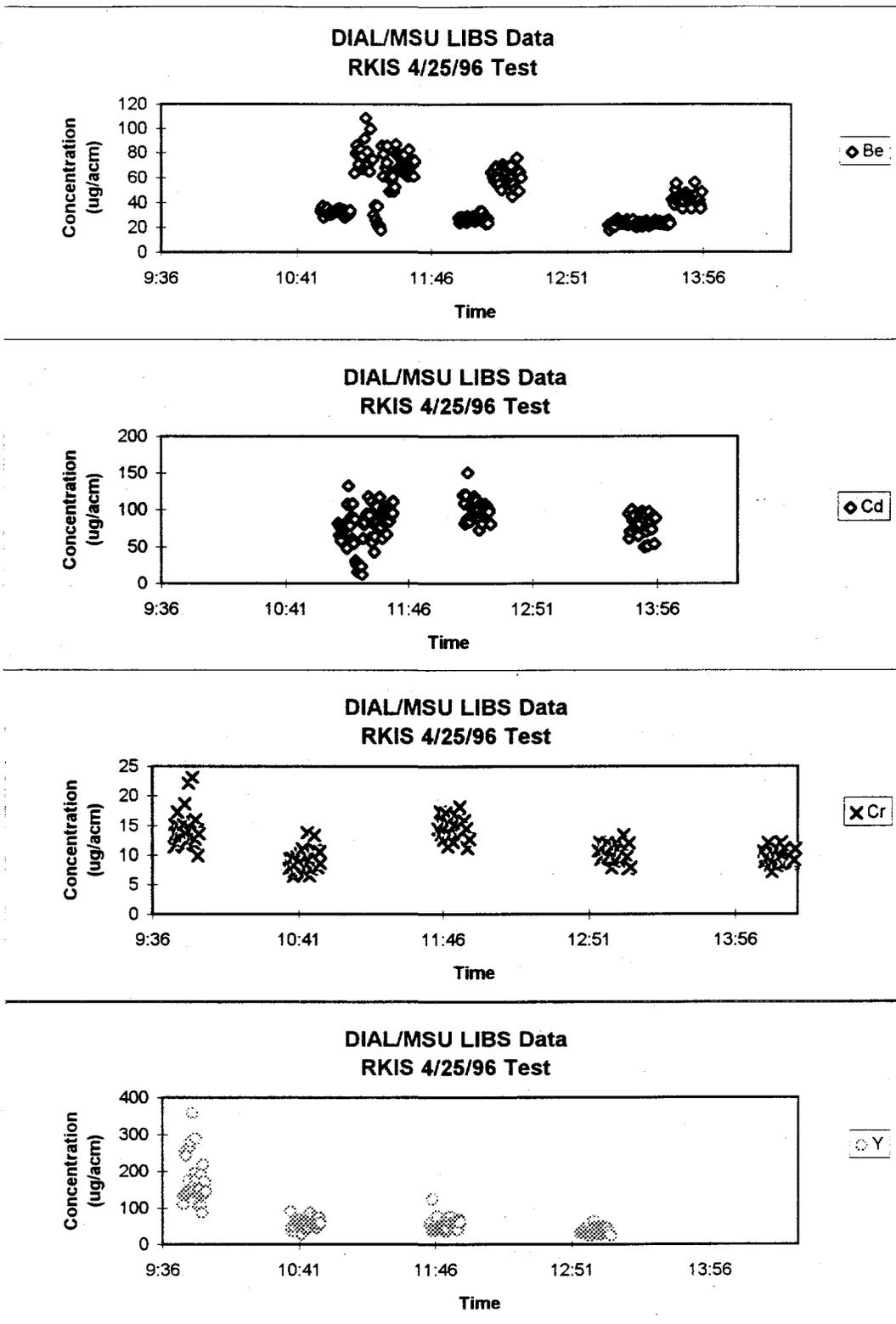


Figure 6
Concentration of Cr, Cd, Be and Y at different times during April 25, 1996 test.

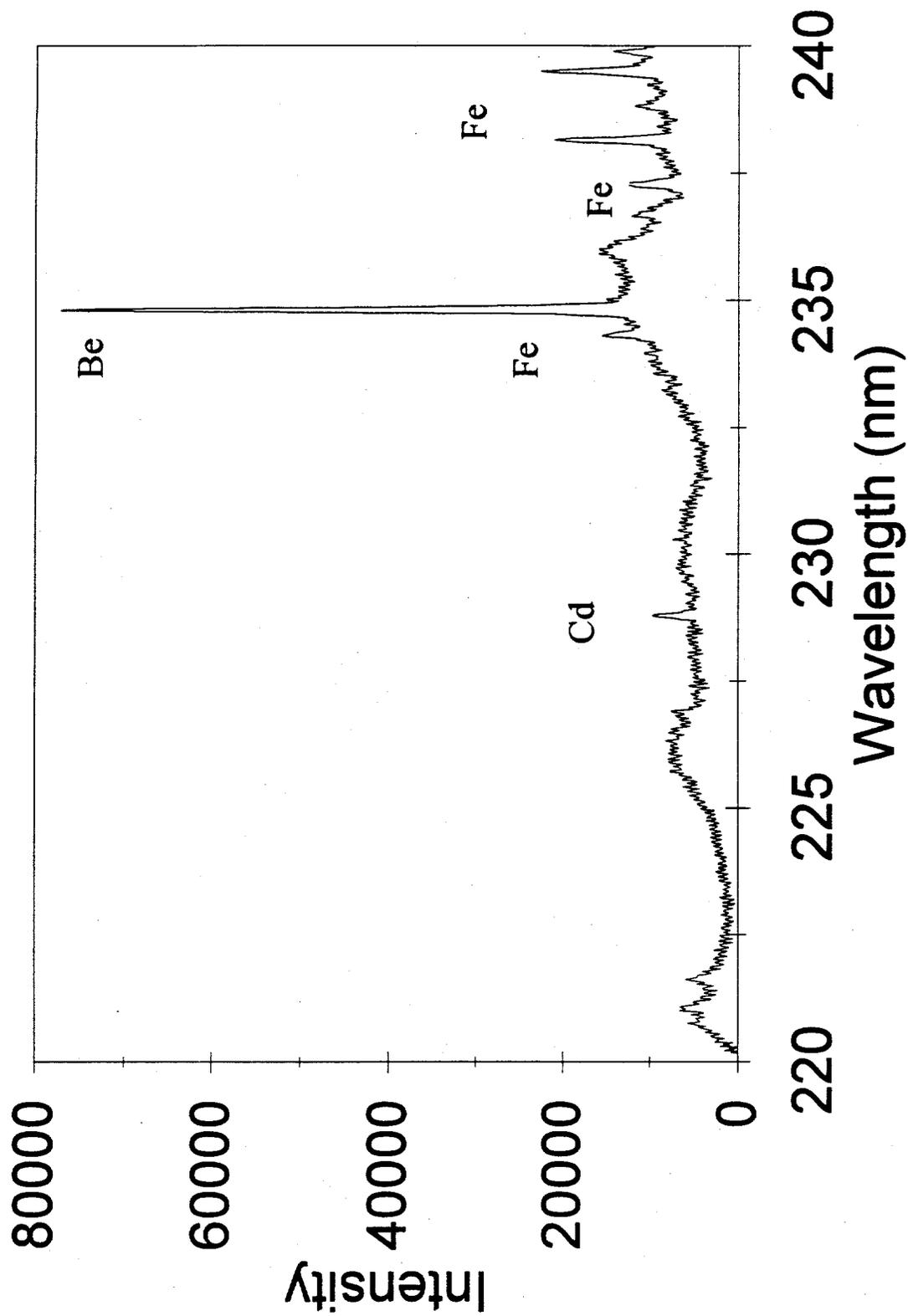


Figure 7
LIBS spectrum in the spectral region of 230 nm.

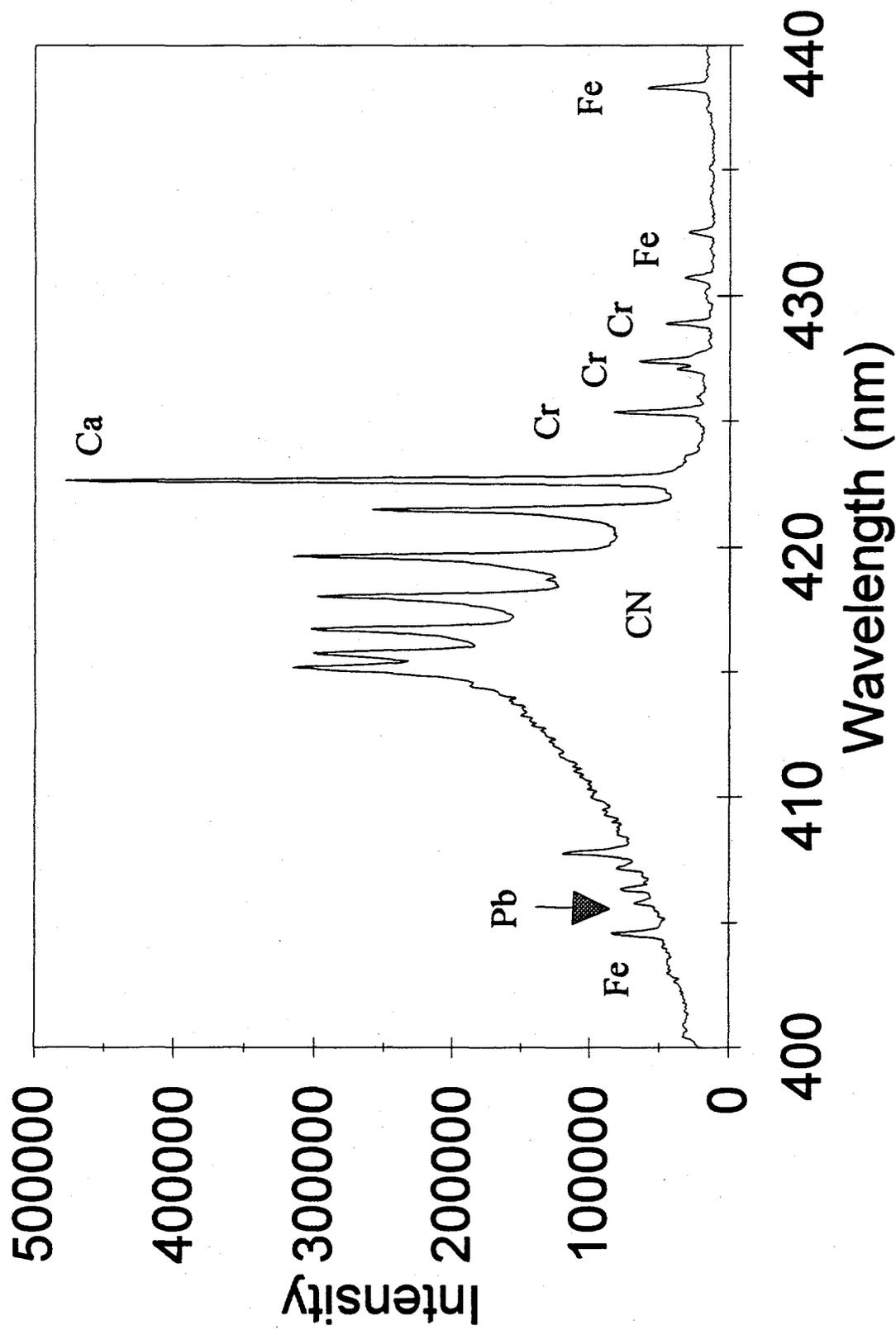


Figure 8
LIBS spectrum in the spectral region of 420 nm.

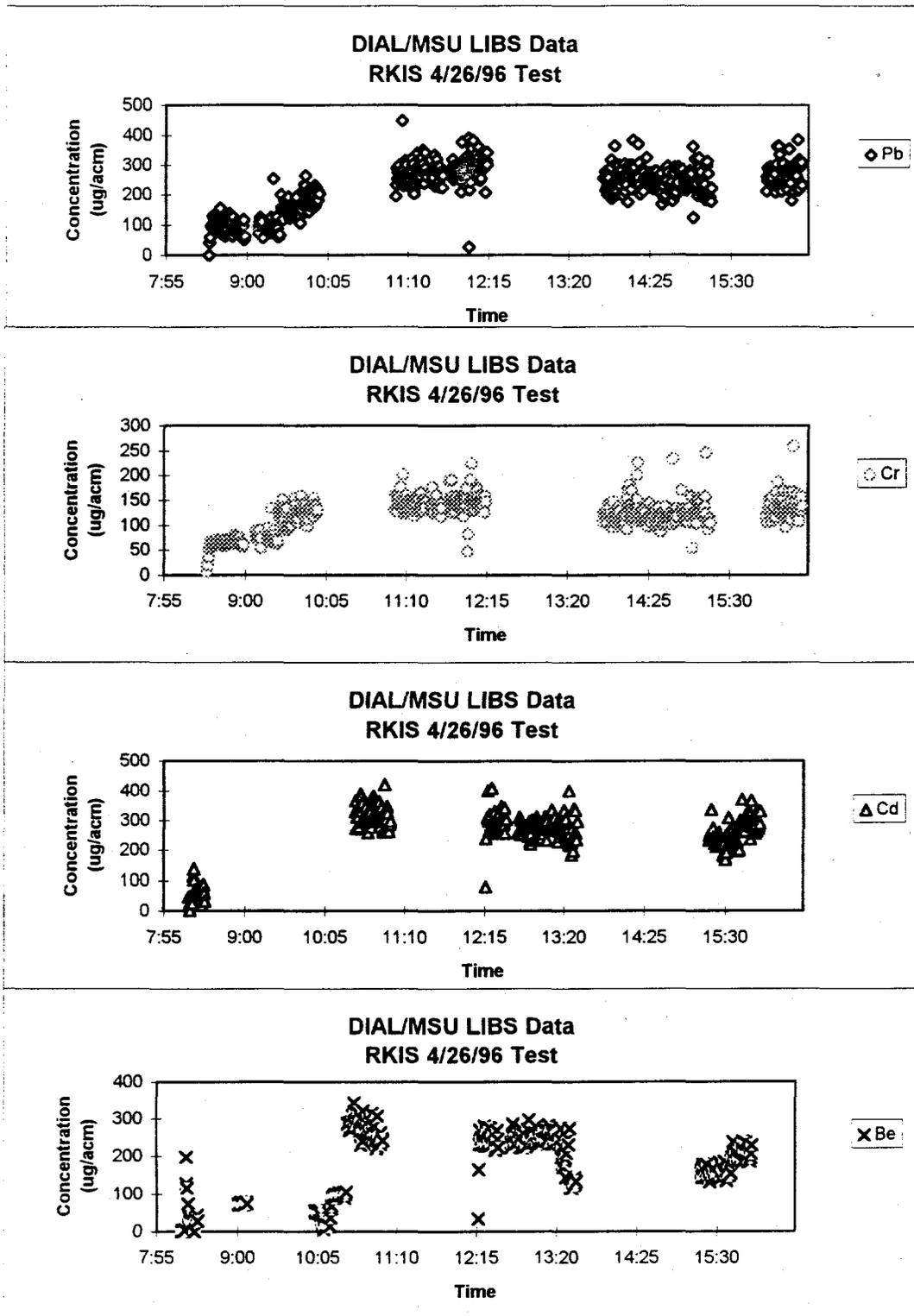


Figure 9
Concentration of Pb, Cr, Cd and Be at different times during April 26, 1996 test.

Appendix A

RKIS 4/22/96 Test

Time		Concentration (ug/acm)			Remark
From	To	Cr	Be	Y	
9:02	9:12		35		34 RM#1: 9:02-9:32 & 10:10-10:40
9:28	9:31			13	
10:10	10:17			23	
11:05	11:19		22		14 Rm#2: 11:05-11:35 & 12:10-12:40
12:10	12:18			20	
13:17	13:27		16		12 Rm#3 : 13:16-13:46 & 14:20-14:33
13:28	13:33			21	
16:15	16:21			21	Rm#4: 15:20-15:50 & 16:15-16:45
16:22	16:32		15		44
17:06	17:17		18		43 Rm#5: 17:06-17:37 & 18:03-18:33
17:28	17:37			20	
18:03	18:09			8	
18:20	18:30		13		25

Remarks: Medium Metals

1. During the one hour EPA sampling, 4 spectral regions were monitored. Each spectral region was monitored for 15 minutes.
2. LIBS data sampling time is 6.7 seconds which corresponds to an average of 66 laser pulses.
3. On site LIBS Calibration for Cr was made on 4/19/96. The data were in good agreement with the calibration data obtained at DIAL.
Therefore, the calibration data obtained in the DIAL laboratory were directly applied to the RKIS LIBS data to infer the metal concentrations.
4. Pb, Be, and Cd are roughly corrected for spectral interferences and background by substrating the data obtained without metal injection.
5. Inferred Cd concentrations are not appropriate being much higher than expected due to problems of strong spectral interference from the Ti(+) line and the Cd stream concentration near the LIBS detection limit.
6. Accurate Pb concentration could not be obtained since the detection limit was near the gas stream Pb concentration.
7. 12:40 - 13:18 : Cleaned window and realigned optics. Nitrogen purge is insufficient due to faulty tank. New one ordered for Tuesday.
8. 13:54 - 14:58 : Detector had condensation problem. Problem solved by increasing detector operating temperature.
9. 18:19 - 18:36 : Signal reduced because the window was getting dirty.
10. Initially, the Y line concentration was ignored since it was not one of the RCRA metals. Since others were reporting the element, the Y line in the same spectral region as Cr was later used to infer Y concentrations.
11. Note because of the long response time between metal injection and a steady state condition, this data is probably not appropriate for direct comparison with EPA method 29.

Appendix B

DIAL/MSU LIBS RKIS 4/24/96 Data Summary

Time FROM	To	Concentration (ug/acm)			Remarks
		Be	Cr	Y	
8:55	9:09		9		RM #1: 8:55 - 9:55 &
9:11	9:24			11	10:21 - 11:21
9:26	9:39		18		
9:42	9:55			15	178
10:21	10:35			10	65
10:37	11:06		18		
11:09	11:20			10	100
11:41	12:04		6		RM #2: 11:41 - 12:41 &
12:06	12:48			9	75
13:00	13:08		14		13:00 - 14:01
13:12	13:41			9	64
13:43	14:00		13		
14:40	15:33		14		RM #3: 14:40 - 15:40 &
16:03	16:39			8	16:03 - 17:03
16:41	17:02		25		
17:35	18:10		23		RM #4: 17:35 - 18:35 &
18:12	18:35			8	19:05 - 20:05
19:05	19:41			8	49
19:42	20:04		20		

Remarks : Low Metals

1. Cr, Be, and Y were monitored from two spectral regions during EPA sampling.
2. LIBS data sampling time was 12 seconds which corresponds to an average of 120 laser pulses between 8:27-8:46.
3. LIBS data sampling time was 18 seconds between 8:26 - 9:41 which corresponds an average of 180 laser pulses.
4. LIBS Sampling time changed to 26 seconds (equivalent to an average of 260 laser pulses) after 9:59 to achieve better signal-to-noise data.
5. In general, each selected spectral region was monitored for ~ 20 - 60 minute during EPA sampling.
6. 11:29 - 11:34: Checked window.
7. 14:15 - 14:30 : Cleaned window and optics.
8. 16:05 -16:10 : Checked window. Window was clean.
9. See also pertinent remarks on &042296&.

Appendix D

DIAL/MSU LIBS RKIS 4/26/96 Data Summary

Time	Concentration (ug/acm)				REMARKS		
	From	To	Cr	Pb		Cd	Be
10:20	10:28					99	RM #2 : 10:20-10:50 & 11:10 - 11:40
10:28	10:50				322	286	
11:10	11:38	140	273				RM#3 : 12:02 -12:32 & 12:50-13:20
12:02	12:14	151	307				
12:16	12:32				291	236	RM #4 : 13:45-14:15 & 14:30 - 15:00
12:50	13:20				276	252	
13:49	14:15	122	253				RM # 5: 15:30 - 16:30
14:30	15:00	118	242				
15:30	15:58				268	185	
15:59	16:28	136	272				

Remarks:

1. Cr, Be, Cd, and Pb were monitored employing three spectral regions during EPA sampling.
2. The initial data starting around 8:30 AM reflected that there was little ash in the gas stream and the metal levels were below specifications. This facility problem was cleared up around 10 AM.
3. Pb concentrations were determined today, since the gas stream concentrations are above our detection limit.
4. LIBS Sampling time was 26 seconds (equivalent to an average of 260 laser pulses).
5. In general, each selected spectral region was monitored for ~15 - 30 minute during EPA sampling.
6. 12:35 - 12:43: Checked window.
7. 13:40 -13:42 : Checked window.
8. Only Cr and Pb were monitored during RM # 4 due to fire alarm.
9. 17:03 - 18:30 : On-site calibration.
10. See also pertinent remarks on Cd from 4/25/96 data.

APPENDIX E

FINAL REPORT OF NAVY/TJA CEM DEVELOPER TEAM

Final Report

Multimetals Continuous Emissions Monitor Test Program

May 1996

submitted by:

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TRACEAIR - Multimetals Continuous Emissions Monitor

Technical Description

Overview

The multimetals CEM developed at NAWC China Lake employs inductively coupled argon plasma (ICP) atomic emission spectrometry to provide sensitive, near-real-time detection of hazardous air pollutant metals. ICP spectrometers are most commonly used to perform elemental analysis on liquid samples. For the present application, a state-of-the-art ICP spectrometer has undergone a series of modifications to permit the introduction of sample stream air. In doing so, the inherent sensitivity, long linear range, and freedom from sample matrix interferences associated with ICP atomic emission spectrometry are exploited for the purpose of detecting and monitoring airborne metals. The ICP spectrometer represents the analyzer portion of the CEM system; equally important is the sampling system.

To ensure that a truly representative air sample is continuously provided to the analyzer, an automated sampling system isokinetically extracts a stream of air from the stack or duct to be monitored. Live measurement of stack velocity, temperature, and pressure permits automatic control of the volumetric sampling rate such that 100 percent isokinetic conditions are achieved at all times. The sample air stream is transported from the sampling probe, mounted in a port on the stack, via a thermostatted sample line to the CEM instrument trailer. The sample line temperature is maintained at a value sufficient to prevent condensation of moisture in the sample line. In this way, the integrity of the sample is preserved. A sampling interface of proprietary design permits a sample air stream to be continuously extracted at the high, often variable flow rates associated with isokinetic sampling, and at the same time, permits periodic introduction of sample air aliquots into the analyzer at the constant, low flow rates required for plasma injection. Upon entering the hot plasma, entrained particulate matter is rapidly vaporized and dissociated into atomic and ionic species and then excited, resulting in emission of characteristic wavelengths of light. A direct-reader spectrometer provides sensitive, simultaneous measurement of atomic emission on up to 61 separate wavelength channels. The Thermo Jarrell Ash TRACE 61-E used as the elemental analyzer for this CEM system employs axial viewing of the plasma to ensure the ultimate in sensitivity. An additional benefit of axial viewing is the relaxation of the requirement of optimizing emission viewing height in the plasma since emission is integrated along the axial length of the plasma. This is especially important in the case of large particulates which require longer residence in the plasma to undergo complete vaporization as a prerequisite to excitation and emission.

The computer-controlled sampling interface permits periodic measurement of stack gas and alternate measurement of clean reference air at selected intervals. The results of stack gas measurements are automatically normalized to dry standard conditions, and the results of the reference air measurements, made at dry standard conditions are then

subtracted from the stack results to generate a net concentration in micrograms per dry standard cubic meter. Alternate measurement of reference air and stack gas allows for the analytically-sound practice of "blank" subtraction. Airborne metal concentrations are updated after measurement cycles of 2 minutes or less. Each cycle includes signal integration on-peak, and at multiple off-peak positions to allow for automatic background correction. Accurate background correction is of the utmost importance due to the complex molecular emission spectral background arising from the excitation of NH, NO, and OH species. More rapid analysis may be achieved at the expense of a modest sacrifice in sensitivity, by reducing the integration time.

Hard copies of data are printed out in tabular form as required, data is stored in a data base format, and trend charts indicating concentration vs. time can be generated. A number of interactive outputs are also available including alarms and a process loop feedback circuit.

At selected time intervals, the analyzer automatically re-profiles its spectrometer and performs calibration QC, zero-drift checks, and a reference air measurement. The CEM analyzer also accounts and corrects for spectral interferences from such concomitant species as Fe and Al which may exist in high concentration in furnace or incinerator effluent. All aspects of CEM operation including analyzer functions and isokinetic sampling are under computer control in a Windows multitasking environment.

Operational Requirements

The entire CEM system is transported in a 24' l x 8' w x 11' h air-conditioned instrument trailer and requires only an electrical hookup and a supply of argon gas to operate. Electrical requirements are 208 V, 70 A minimum, single phase. A 40-foot electrical cable is available for connection to a power source. A stack sampling port of at least 3" is required to accommodate the heated sampling probe. Depending on the stack velocity encountered, a selection of calibrated sampling nozzles of different diameters is available. Stack temperatures up to 500 °F and high moisture contents can be tolerated by the present sampling system. For higher temperatures, a different probe is required.

Performance

Of the several analytical techniques presently under consideration for continuous emissions monitoring of hazardous air pollutant metals, ICP atomic emission spectrometry offers the best combination of speed and sensitivity for this application. Although the analytical performance of the argon plasma as an atomization and excitation source is slightly compromised by the necessary introduction of sample air in the present application, detection sensitivity has been achieved that is unprecedented by competing technologies. The presence of air in the argon plasma dramatically increases thermal conductivity and promotes vaporization of particulate matter.

The CEM system described here carries out analytical measurements in the near-real-time regime. Its response time, despite the need to transport the sample stream over a finite distance from the stack to the analyzer, is more than adequate to provide analytical results in the timely manner expected.

This CEM system is tolerant of relatively high moisture and particulate loading, and is immune to deleterious effects of combustion exhaust gases in stacks where conditions are not extremely acidic or caustic. The CEM described here is specifically designed to detect hazardous air pollutant metals including Ag, As, Ba, Be, Cd, Co, Cr, Hg, Mn, Ni, Pb, Sb, Se, and Tl. Numerous other airborne metals can be detected by simply installing the appropriate detector channels in the spectrometer. The ICP spectrometer is a direct reader and is presently configured to simultaneously all of analyze the metals listed above plus additional elements such as Fe and Al, which are potential spectral interferences, and Y and Mg, elements useful for optimizing plasma and spectrometer performance. ICP atomic emission spectrometry has the distinct advantage of having a long linear dynamic range of detection because of the spatially-uniform excitation properties of the plasma. Other excitation sources suffer from effects such as self-absorption of radiation which severely limit their linear range.

Detection limits for the 14 hazardous air pollutant metals listed above have been determined using the method prescribed in the EPA's draft performance specifications for multimetals CEMs. After calibration of the system, 7 replicate measurements are made while introducing clean (blank) air. The concentration value in $\mu\text{g}/\text{DSCM}$, equivalent to 3 times the standard deviation of the 7 replicate measurements is taken as the detection limit. The detection limit therefore, is that analyte concentration at which the detected signal to noise ratio is 3. Although the detection limit is not a practical quantitation limit, it is a valuable figure of merit for comparing the performance of different systems. In the present case, the overall system sensitivity is determined by the limiting noise inherent in the sampling system as well as the analyzer. The detection limits, representing analyte concentrations giving a signal-to-noise ratio of 3, estimated for the 14 hazardous air pollutant metals, in the manner described above are presented below:

Detection Limits in micrograms per dry standard cubic meter

	Be .02																	
					Cr .2	Mn .03		Co .2		Ni .07				As 2.2	Se 2.0			
										Ag .2	Cd .03			Sb 3.3				
	Ba .02										Hg 5.0	Tl 3.0	Pb .3					

Linear dynamic ranges for most elements extend 4-5 orders of magnitude allowing high concentration as well as trace detection of hazardous air pollutant metals.

Many of the innovations employed in this prototype multimetals CEM system are the subject of a patent application, U.S. Navy Case Number 76669. The principal investigator and his industrial partner, Thermo Jarrell Ash Corporation, presently have a Cooperative Research and Development Agreement in place. This agreement was signed under the auspices of the Naval Air Warfare Center Weapons Division Technology Transfer Office and the Office of Naval Research. The Navy/TJA concept has been developed under both Navy and Army sponsorship.

Applications

The multimetals CEM system described here was designed and constructed for the specific purpose of metal emissions monitoring and pollution prevention for explosive ordnance demilitarization furnaces. The inherent versatility of this approach however, makes it suitable for many non-military applications in which enhanced monitoring of the metals emissions from boilers, incinerators, and furnaces is required. The ability of this system to generate a nearly instantaneous indication of compliance status provides the user with unprecedented ability to initiate remedial actions in the event of impending non-compliance.

Standard Operating Procedure

Preparations

One or two hours prior to actual monitoring, the sampling probe must be installed in the stack and all pneumatic connections must be made and appropriate leak checks carried out, much in the same manner as with EPA Methods 5 or 29. Differential pressure measurements using pitot tubes mounted on the sampling probe can be used to optimize the position and orientation of the probe nozzle in the stack. Power is then switched on to provide heating to the sample probe and sampling lines. The sampling interface, mounted directly on the ICP instrument cabinet, is also thermostatted and its temperature is allowed to equilibrate prior to monitoring. The automated isokinetic sampling system is activated and operation is confirmed. The ICP analyzer requires only 20-30 minutes to warm up and during that time, a number of diagnostic and optimization steps may be carried out.

Calibration

Calibration consists of introduction into the CEM of metal-containing aerosols of known concentration at dry standard conditions. Aerosols are generated using an ultrasonic nebulizer with desolvation. The generated aerosols are mixed and diluted with ambient air. Aerosol concentration is determined by dividing the aerosol generator output rate by the total air flow rate in which the aerosols are mixed. The aerosol generation system used is similar to several reported in the literature but the methodology has been refined for the present application. The aerosol generator was rigorously characterized in the laboratory to ascertain the value and repeatability of its output efficiency. Filter capture and subsequent analysis of these aerosols provides quality assurance and a confirmation of the validity of the calibration procedure. Prior to calibration, the spectrometer is profiled to ensure maximum sensitivity for all elements. Several diagnostic tests are performed to confirm stable plasma operation and sample injection. Multiple calibration standards are used for each element resulting in calculation of a linear calibration curve. A minimum correlation coefficient of 0.995 is required for each element.

Prior to monitoring, operating conditions are first optimized and then an aqueous calibration QC check solution is introduced into the plasma by conventional pneumatic nebulization. Measured values are compared with those measured for the same solution at the time of calibration. The slopes or intercepts of calibration curves for each element are automatically normalized within reasonable limits to account for slight variations in operating parameters such as atmospheric pressure or slight optical misalignment in the spectrometer. Periodically throughout the monitoring process, the spectrometer is re-profiled and the QC solution is analyzed and necessary adjustments are automatically made. The object is to obtain a high degree of accuracy. Trend charts are routinely plotted to illustrate both QC and zero drift compliance. The default occurrence for QC and zero drift measurements are once per hour but measurements can be made more or less frequently if required.

Signal Processing

Although sample air is extracted isokinetically on a continuous basis, sample air is introduced into the plasma periodically. The interface is designed in such a way that upon computer command, a steady-state flow of analyte aerosol enters the plasma and its flow is sustained for approximately 60 seconds. This is sufficient time for the spectrometer system to perform both on-peak emission measurements, and emission measurements at selected off-peak positions for the purpose of spectral background correction. At the end of the 60 second period the integrated intensities for each element are compared against calibration curves of intensity vs. concentration. Calculations that take into account the temperature, pressure, and moisture content of the sample air entering the plasma are used to normalize the concentration values to standard conditions. Reference air measurements, made at standard conditions are then subtracted from the standardized stack gas metal concentrations to yield net airborne metal concentrations in units of micrograms per dry standard cubic meter. Optionally, the concentration can be normalized to 7 percent oxygen by importing a signal from an oxygen analyzer or by manual data input to correct for deliberate or inadvertent dilution of the sample stream.

Advantages

The multimetals CEM system described here is intended to provide nearly instantaneous measurement of a wide range of hazardous air pollutant metals with sensitivity comparable to reference methods such as EPA Methods 5 or 29. This system offers the unique advantage of providing results in the rapid time frame required to facilitate effective pollution abatement efforts. As a result of several technical innovations, the argon ICP analyzer is amenable to the introduction of sample stream air sampled isokinetically at relatively high flow rates that favor efficient transport over moderate distances between the stack and the analyzer/interface. Consequently, the proven advantages of ICP atomic emission can be fully exploited. As presently configured, the CEM system can provide, on average, 30 or more analyses per hour depending on the integration time per sample and the frequency of QC checks. At this time, it is not prudent to make claims regarding accuracy and precision, since the proposed field tests are an opportunity to assess these figures of merit. Preliminary goals for accuracy and precision are $\pm 20\%$ and $< 5\%$ RSD, respectively. The CEM system produces a minimum of liquid waste, on the order of less than one liter in an eight hour working period.

Limitations

Despite the inherent sensitivity of this system, conventional reference methods retain an ultimate sensitivity advantage by virtue of their integrative nature. However, this sensitivity comes at the expense of timeliness; i.e., the longer the period of sample collection - the more sensitive. A survey of emerging technologies for metals CEMs illustrates that in most cases, high speed and high sensitivity are mutually exclusive goals. As stated earlier, ICP atomic emission spectrometry, as embodied in the system described here, represents the ideal compromise in which both appreciable speed and sensitivity are realized.

All CEM technologies that employ detection of atomic emission are subject to spectral interferences from concomitant species such as Fe and Al. Failure to effectively correct for these interferences will undoubtedly lead to gross inaccuracies in measurement and a dramatic reduction in actual sensitivity for affected analyte elements.

The CEM system described here is a prototype and is not yet optimally packaged and completely ruggedized for operating in harsh environments. Consequently, it is presently transported in a trailer to provide some degree of mobility, climate control, cleanliness, and security. This system requires certain consumable items, primarily argon, which presents the most significant operating expense, approximately \$3-4 per hour of operating time. The CEM system and the trailer in which it is housed, require an electrical supply to sustain the plasma, operate various components of the sampling system, and air condition the trailer.

Because of the long linear dynamic range inherent to ICP atomic emission, the upper concentration limits are rather high. However, these limits are determined to a certain degree by the lower limit of detection and are typically 4-5 orders of magnitude greater. Linear response to metal aerosol concentrations as high as 5000 micrograms per cubic meter has been demonstrated in the laboratory.

At present, it is desirable for an ICP specialist to operate the system but a technician with a certain amount of hands-on training can also successfully operate the system. The ultimate goal for this system is to provide turnkey operation.

In the spirit of technology transfer, the Navy, in conjunction with its industrial partner, Thermo Jarrell Ash Corporation, is in the process of conceptualizing the next generation multimetals CEM system using technologies specifically developed for the present prototype system, recent breakthroughs in ICP spectrometer technology, and user-, and regulatory-driven performance requirements. This concept will incorporate both analyzer and sampling capabilities in a compact, user-friendly package.

Results of Field Testing

April 22-26

QA/QC Procedures and Results

The TRACEAIR Navy/TJA-developed multimetals CEM incorporates a number of automated QA/QC features to ensure constant sensitivity, repeatability, accuracy, and precision. Following the introduction of calibration aerosols, curvefit calculations are carried out to obtain a linear fit of signal intensity vs. aerosol concentration data for the multi-standard calibration procedure. Typically, a correlation coefficient of 0.9999 is achieved for most metals owing to the precise operation of the TRACEAIR sampling interface. A minimum of 0.995 is required or calibration for a given metal will be repeated. Immediately following the curvefit calculation, an aqueous QC solution containing the metals of interest is pneumatically nebulized into the plasma and emission measurements are made for each metal. The measured values are then recorded in a QC table for later use. These values serve as a benchmark for later QC checks to ascertain the degree of instrument drift and to facilitate necessary corrections.

Repeatedly throughout the monitoring process, the program pauses to allow the spectrometer to be automatically reprofiled and a calibration QC check to be carried out. An aqueous solution of arsenic is introduced into the plasma and a spectral profile of the arsenic emission line at 189.0 nm is obtained. If the peak of that line has drifted slightly from its original position, an automatic correction is made to reprofile the spectrometer. This ensures both constant accuracy and sensitivity. Following the reprofile, the aqueous QC solution is introduced. The solution is analyzed and the results are compared against values previously stored in a QC table. If the results do not agree within a certain tolerance, a process called QC normalization is initiated, where coefficients are calculated, stored, and applied to all subsequent determinations in a manner that preserves the sensitivity (slope) recorded at the time of calibration. A tabulation of the QC status (pass/fail) is printed out for each element. After the reprofile and QC calibration tests are complete, monitoring is resumed.

At the end of each day or period of monitoring, additional QA/QC checks are made. First, a zero drift test is conducted. Here, the goal is to generate a zero or near-zero readout for the introduction of clean reference air, in the absence of metals. If the detected concentration is within a certain tolerance of zero (usually determined by some factor times the detection limit for a given metal), the test is considered a success. Upon failure of the zero drift test, the results are noted and recorded for future consideration. No zero drift test failed during the week of April 22-26. Following the zero drift test, an additional QC calibration test is conducted in lieu of a "span check". A classic span check is not necessary in the present case because of the extremely long linear dynamic range associated with ICP atomic emission spectrometry. It would not be prudent nor practical to introduce a span concentration of 5000 micrograms per cubic meter or greater. The aqueous QC solution contains metal concentrations that when introduced into the plasma,

approximate airborne metal concentrations well within the linear range of the CEM system. Measuring these signals is adequate to confirm span agreement since the calibration curve is linear over 4-5 orders of magnitude of concentration. No final QC calibration check failed during the week of April 22-26.

Tabulation of Field Data

Monday, April 22, 1996

Element	Sb	As	Be	Cd	Cr	Fe	Pb	Hg	Se	Y
RM1-1	95.8	117.6	66.6	80.2	60.8	3292	80.6	9.3	59.4	136.5
RM1-2	159.7	167.2	140.2	128.1	91.4	2385	124.1	30.8	63.0	245.7
RM2-1	138.0	143.7	93.1	101.4	75.4	2093	110.5	34.6	58.2	182.2
RM2-2	120.4	143.5	83.8	78.9	42.0	1567	77.2	21.2	65.1	179.8
RM3-1	90.2	102.7	63.9	64.9	38.5	1435	64.6	6.7	59.8	133.3
RM3-2	97.9	114.6	71.7	75.0	47.5	1472	86.7	20.7	104.7	160.3
RM4-1	89.1	112.9	64.8	65.1	41.8	1002	71.2	9.6	123.1	121.7
RM4-2	122.7	149.3	89.4	85.3	52.0	1370	85.6	9.3	96.8	187.7
RM5-1	150.0	198.7	109.1	120.3	57.5	1335	94.4	10.7	76.7	207.6
RM5-2	87.9	142.1	55.1	54.8	39.6	1581	77.4	11.9	85.9	173.3

Wednesday, April 24, 1996

Element	Sb	As	Be	Cd	Cr	Fe	Pb	Hg	Se	Y
RM1-1	N/A	N/A	N/A	N/A						
RM1-2	65.5	40.5	26.3	19.5	18.1	2104	15.0	3.6	37.3	205.7
RM2-1	46.4	55.8	21.1	15.0	14.3	2027	12.0	3.0	57.8	189.1
RM2-2	59.6	65.1	31.0	22.5	20.7	2720	17.5	2.6	67.0	230.3
RM3-1	59.3	72.4	30.3	22.1	20.8	2519	19.0	1.8	76.5	253.5
RM3-2	59.8	73.7	29.6	22.2	20.7	2468	18.2	2.1	72.7	247.8
RM4-1	49.1	73.7	45.6	19.0	19.9	2393	16.3	1.9	86.3	232.0
RM4-2	49.6	58.0	24.7	18.0	17.2	2317	14.7	1.8	82.2	227.7

Thursday, April 25, 1996

Element	Sb	As	Be	Cd	Cr	Fe	Pb	Hg	Se	Y
RM1	181.1	178.9	144.5	116.2	32.4	2444	64.8	24.2	112.1	208.6
RM2	172.2	186.6	145.6	116.8	31.7	2219	61.9	19.1	111.7	215.7
RM3	200.2	76.7	149.6	116.4	31.1	1796	57.3	16.6	45.4	228.3

Friday, April 26, 1996

Element	Sb	As	Be	Cd	Cr	Fe	Pb	Hg	Se	Y
RM1-1	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
RM1-2	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
RM2-1	1047	804	1136	824	196	2401	433	66.3	119	155
RM2-2	1035	837	1014	823	204	2799	426	67.3	118	143
RM3-1	932	814	1026	711	165	2513	374	74.9	117	136
RM3-2	988	879	1089	749	163	2529	408	74.4	126	144
RM4-1	1206	959	1248	889	190	3061	481	81.4	95	160
RM4-2	1129	894	1204	797	175	2647	436	78.4	90	159
RM5	1029	800	1073	755	141	2786	319	71.8	90	144

Data Interpretation

It is important to note that one of the unique functions of the TRACEAIR multimetals CEM is to generate results that are already normalized to dry standard conditions and corrected to 7 percent oxygen. Knowledge of the temperature, pressure, moisture content, and percent oxygen in the sample air introduced into the plasma is required in order to accomplish this task. These values can either be obtained from appropriate transducers mounted in the sampling interface (temperature and pressure) or obtained from gas CEMs (moisture and oxygen). It is our intent to measure the latter parameters independently on future outings. For the present test, moisture and oxygen values of 6 and 16 percent respectively, were assumed, based on readings provided by Paul Lemieux. Post-test data manipulation was, for the most part, limited to selecting the appropriate data points that coincided with Method 29 runs and tabulating them in a Lotus123 spreadsheet to facilitate reporting. Data reported for Monday, April 22, for arsenic was subjected to a post-test spectral subtraction to account for spectral interference from molecular spectral interference not previously observed in clean reference air. An alternate but equally sensitive arsenic wavelength was selected for all subsequent

measurements and no such interference was noted. In confirmation of the presence of nascent molecular species in the stack gas, we routinely observed the classic violet emission of the CN radical in the ICP. The most likely source of CN is a reaction between NO_x species and hydrocarbons in the stack gas.

All data is reported therefore in units of micrograms per dry standard cubic meter corrected to 7 percent oxygen. No further corrections are necessary. We believe this practice to be within the true spirit of so-called real-time field measurements. Throughout each test day, we continuously recorded concentration data for up to 17 different metals simultaneously, including those that were constituents of fly ash. For each period of time that Method 29 was sampling, we tabulated coincident data points for each metal of interest. A simple average was taken of all tabulated values for each metal for reporting and Method 29 comparison purposes.

It is important to note that although the Navy/TJA CEM is capable of making repeated measurements at intervals of 2 minutes or less, the measurement timing sequence was altered for the recent tests to allow for more frequent blank subtractions in light of the fact that emission in the plasma from unknown molecular species was observed. Although we were not prepared at the time to carry out a running subtraction of these features, we endeavored instead to acquire sufficient net emission data to facilitate study of this phenomena in the future.

The effects of spectral interferences between iron and aluminum, present in large concentrations due to fly ash introduction, and the target metals, are well documented in the ICP literature and have been a routine observation in our previous experience. An additional unique feature of our CEM system is its ability to accurately account and correct for these interferences. Failure to do so would incur a serious inaccuracy penalty. For example, the spectral interference imposed by iron on mercury is rather appreciable, however, our system was able to correct for this interference as part of its routine calculation procedure. (please see Figure 6 in APPENDIX).

Response Time

For the present tests, the Navy/TJA CEM system was mounted in a trailer that was parked outside the High Bay G adjacent to the area where the rotary kiln was located. This necessitated the use of a 75-ft heated sample line to transported extracted air from the stack to the CEM. The approximate flow rate of sample air, required for isokinetic extraction under the present set of stack conditions, was 8.8 SLM. This translates to a linear velocity of 5.7 ft/sec through the 0.41" ID sample line. Accordingly, an extracted portion of sample air takes approximately 21 seconds to traverse the combined lengths of the sample probe (4'), the heated sample line (75'), and the sample loop contained within the sampling interface (40'). The sample traverse time is small when compared with the duration of the measurement cycles used in the present test (3.5 minutes). Consequently, sample transport adds no appreciable delay to data collection and measurement response time is a function of the measurement duration only. As stated above, we opted to

generate measurements at 3.5 minute intervals rather than every 2 minutes as is possible with our system. The data presented in many of the figures included in the APPENDIX attests to the rapid response time that was demonstrated. In each case, it is evident that within the span of 2 subsequent measurements, the Navy/TJA CEM indicates an excursion from baseline to full scale. The sensitivity of the Navy/TJA CEM to transient events proved invaluable during the week of April 22-26 in assisting the EPA/Acurex individuals responsible for metal introduction and Reference Method testing, in knowing exactly when stack metal levels had approximated a steady state. Such was not the case in many instances when Method 29 was being carried out, raising some doubt as to the validity of relative accuracy comparisons between the CEM systems and the reference method for those instances. Figure 1 in the APPENDIX illustrates this point very well. It is interesting to note that on occasion, when the metal stream was turned on, a large spike or overshoot was observed by our system. This behavior is evident in Figure 2 in the APPENDIX. Observations made throughout the week of April 22-26, and a post-test inspection of our data indicates that despite erratic metal introduction on the morning of April 22, enhanced control over this process was achieved during subsequent tests. It was pointed out by Dr. Paul Lemieux that the Navy/TJA CEM would have been an invaluable asset to the EPA/Acurex team during the preceding weeks of preparation for this test as a means of helping optimize the metals introduction process.

Data Quality

It is not possible to comment about measurement accuracy at the present time due to the unavailability of reference method data. However, assessments of a qualitative nature can be made by inspecting the data, observing certain trends, and evaluating the degree of consistency between measurements. At certain times during the test schedule, the rate of metal introduction and associated stack emissions were fairly constant. During these times, data from the Navy/TJA CEM shows a high degree of repeatability and precision for most metals, especially those introduced in aqueous form. For example, the results recorded during the 3 reference method intervals on Thursday, April 25 indicate a high degree of measurement repeatability. Relative standard deviations less than 5% were calculated for agreement between the results of 3 reference method trials for several elements. A RSD of less than 1% was calculated for cadmium for the 3 trials. Similar repeatability was noted for the results obtained on April 24 and 26 as well.

Clearly, those metals present as components of fly ash exhibit widely-varying concentrations in the stack gas over time. This is well illustrated in Figure 6 where iron data shows considerable scatter. Similar scatter is evident in data recorded for other fly-ash borne elements such as aluminum, barium, and manganese (Figs. 9-11). The high degree of correlation between the data points shown in Figs. 9-11 suggest that the data scatter is source related, i.e., inability to achieve a steady state introduction and transport rate for the fly ash. As this may not have been a goal of the present test, the resulting data obtained for fly ash metals lends further proof of the Navy/TJA CEM's sensitivity to transient changes in stack metal concentration.

Self Assessment

CEM Test Program

The test program was an overall success in our opinion and a great opportunity to carry out a side-by-side comparison of metals CEM prototypes. The test program was well planned and executed to the extent that challenging, but reasonably controlled conditions were achieved, i.e., fly ash, moisture, temperature, etc.. The EPA and Acurex were excellent hosts and should be commended for their efforts.

Navy/TJA CEM System

The performance of the Navy/TJA CEM system during the DOE/EPA test program was particularly gratifying to the developers. The goal of the present effort was to integrate the reliable sampling capabilities of EPA Method 29 (isokinetic extraction, etc.), the detection capabilities of a state-of-the-art ICP spectrometer (sensitivity, freedom from sample matrix interferences), and sound analytical practices including frequent blank subtraction and the use of certain QA/QC protocols to ensure constant sensitivity, reasonable accuracy, and good precision. By incorporating these features, our aim was to achieve definitive results to facilitate the conclusion that at least one emerging metals CEM technology is sufficiently mature and adequately promising to warrant continued interest and possible support. With due consideration to the fact that a relative accuracy assessment is not yet available, we believe that we have achieved the stated goals. We are prepared to aggressively investigate any accuracy discrepancies with the intent of rectifying them prior to future field work. As with any of the technical challenges previously encountered, we are confident that a systematic approach to identifying the problem will ensure a positive outcome.

Strengths:

Notable achievements during the recent test program that exemplify the excellent capabilities of the Navy/TJA CEM system are as follows:

1. Continuous, often unattended operation of the Navy/TJA CEM throughout the week.
2. Ability to detect *all* target metals simultaneously on a continuous basis at all concentration levels presented, plus fly ash metals.
3. Automatic correction for spectral interferences from iron and aluminum.
4. Rapid response of measurement system to transient changes in stack metals concentrations.

Strengths (cont'd)

5. Tolerance of stack moisture and particulate loading.
6. On-line correction of data to dry standard conditions and 7 percent oxygen.
7. Navy/TJA CEM operation required minimum human activity at stack and immediate vicinity.
8. Considerable value of data in facilitating operation of rotary kiln and metals introduction.
9. General ease of setup and operation; high level of instrument automation; minimal manpower requirements.
10. All components of the Navy/TJA CEM system performed together exactly as designed despite the fact that this was the first "real-world" test opportunity for this system as a whole.

Weaknesses:

1. The use of a heated sample line to transport a continuous stream of sample air from the stack to the CEM is a potential weakness due to the possibility of sample loss arising from frictional forces, adsorption to tubing walls, and general particulate settling. Every attempt has been made to select operating parameters that minimize the probability that such losses may occur. Previous experience on our part and that of colleagues in Europe indicates that when careful optimization is carried out, losses of this type are indeed minimized so as not to contribute an appreciable error to the analysis. To evaluate potential sample losses in the heated sample line, a post test acid rinse of the sample lines and sampling probe will be conducted to quantitatively recover any residual metallic species. The rinseate will be chemically digested and spectrochemically analyzed to ascertain the extent of sample deposition in the system.
2. Until an assessment of relative accuracy is available, additional weaknesses cannot be speculated upon. The relative accuracy of the Navy/TJA CEM during the recent tests will reflect directly on a number of important cornerstones of this technology including calibration; sample collection and transport; signal processing, quantitative analysis and data handling; and the ability of the analyzer to discriminate against spectral interferences from both concomitant metals such as iron and aluminum, and from stack gas molecular species. Failure to achieve reasonable relative accuracy will present challenging tasks to the developers to carefully identify and correct any error-contributing factors or forces.

Lessons Learned:

1. Considering the requirement during the present test, that data be submitted in a specific format, it would have been worthwhile, in retrospect, to have additional computing capability on hand so that one PC could be dedicated to automating CEM and sampling functions and another PC could be available for preparing data for submission. Although the system as presently configured provides printouts of data every few minutes, the requirement that data be submitted in a specific format naturally made the process more labor intensive. It is proposed that data handling be further automated, possibly by passing raw data from one PC to another, to expedite data availability in alternate forms.

2. We have recognized in the past that "real-world" stack conditions are not always approximated by laboratory conditions. For example, the observation of molecular emission adjacent to some of the atomic emission lines was somewhat unexpected. In one case, we were able to circumvent this problem by detecting arsenic at an alternate emission line. We recognize the limitations posed by using a spectrometer equipped with a limited number of analytical detectors installed. The obvious solution is to install additional detectors to permit use of alternate atomic emission lines in the event of coincident molecular emission arising from nascent molecular species in the stack gas. The accelerated schedule for preparing for this test did not allow time for laboratory experimentation to determine the analytical effects of gases such as NO_x and hydrocarbons in the sample air. However, this will be the subject of a future investigation.

3. Prior to the tests, we experienced an equipment malfunction related to possible damage incurred during transport of our instrument trailer. Mobilization and cooperation of several individuals at TJA resulted in this problem being overcome in a timely fashion. Additional care in securing various components in the trailer for long-distance transportation will be essential in avoiding a repeat of this type of problem on future outings.

Recommendations for Future Work:

In general, it will be desirable to streamline and simplify various aspects of operation whereby human effort is minimized and more reliable, automated action is maximized. It will be advantageous in the future to more accurately account for spectral contributions due to molecular gases in the stack and nascent molecular species formed in the stack or in the plasma. It is important to note that the contributions of these species is not negligible considering the high sensitivity and very low detection limits achievable by the Navy/TJA system. In the interest of measurement accuracy, it will be worthwhile to establish a provision to record and account for these contributions and facilitate automated correction.

Conclusion:

The potential for the Navy/TJA CEM concept is obvious. The full capabilities and limitations of this approach can only be identified by rigorous field evaluation under a wide range of conditions. The developers welcome future opportunities to demonstrate this promising technology and identify its ultimate strengths and weaknesses. In designing and assembling this system, the developers have done so with due consideration to the draft performance specifications and QA/QC requirements outlined by the EPA Office of Solid Waste for multimetals CEM systems. We believe that the recent test provided a valuable opportunity to demonstrate that the performance of the Navy/TJA CEM system was consistent with the expectations of the developers as well as the projected requirements of regulators and potential users.

APPENDIX

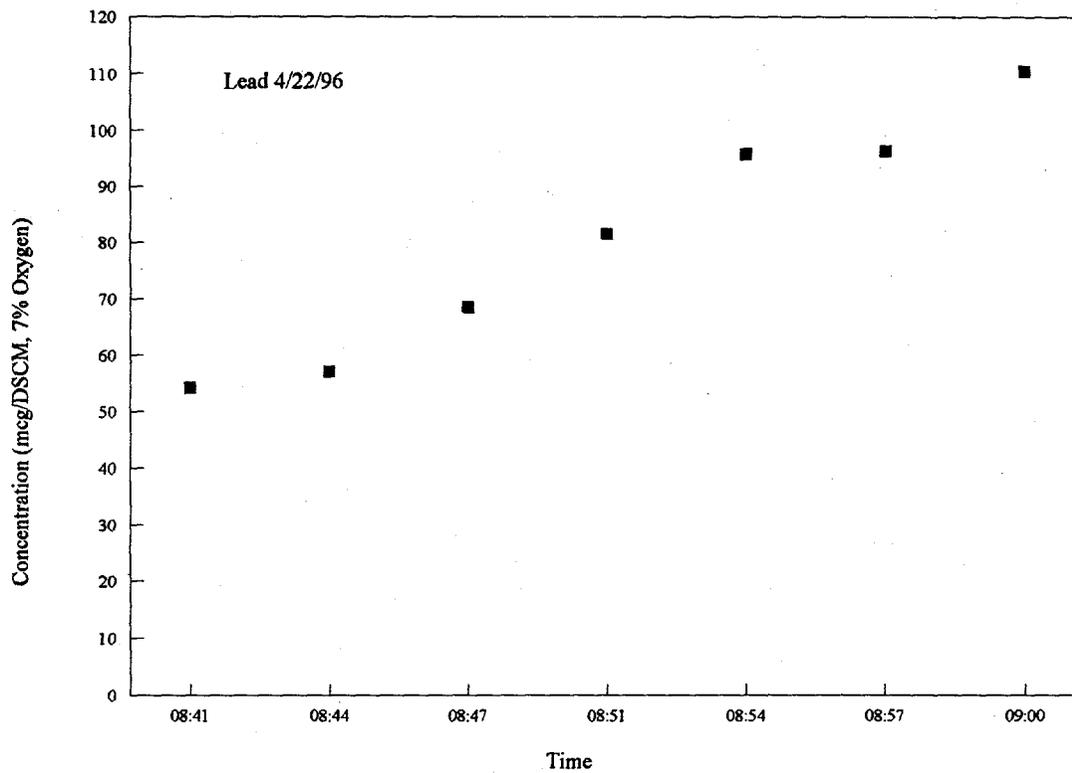


Figure 1. Lead data from 4/22 illustrating failure to achieve steady state metals introduction into rotary kiln. Method 29 was initiated at 08:40. Average CEM value for lead (08:41 - 09:00) was 80.6 mcg/DSCM, 7% O₂.

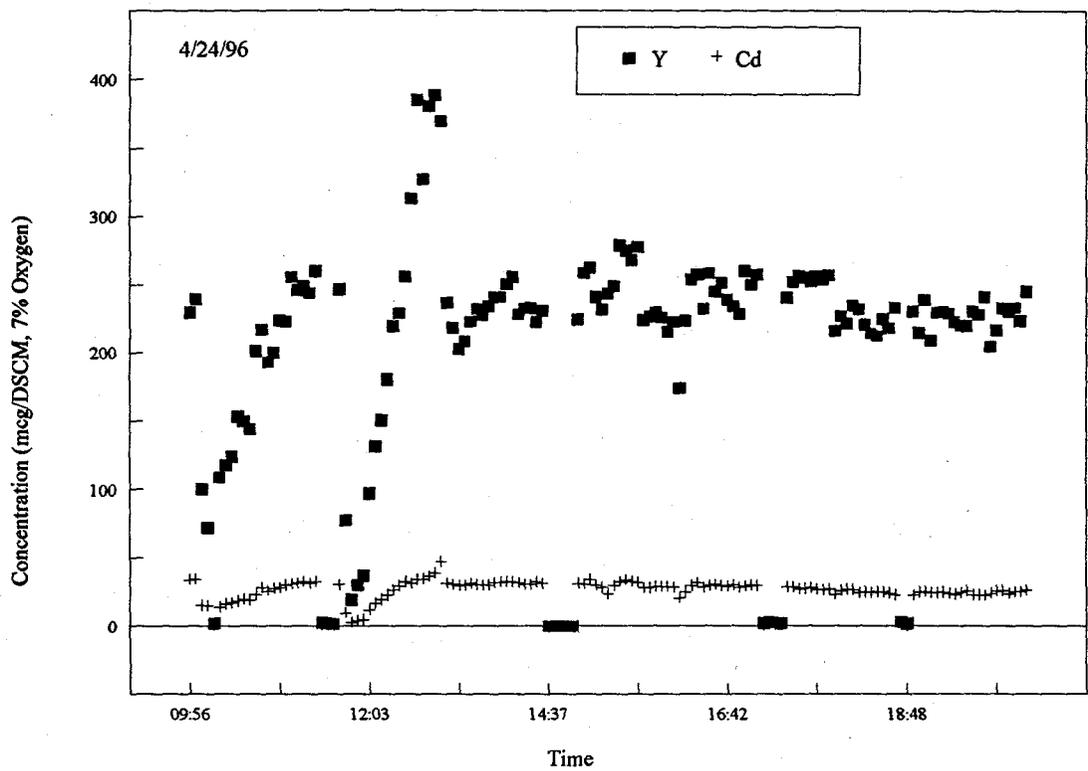


Figure 2. Superimposed yttrium and cadmium data from 4/24 illustrating correlation between the apparent concentrations of the two elements.

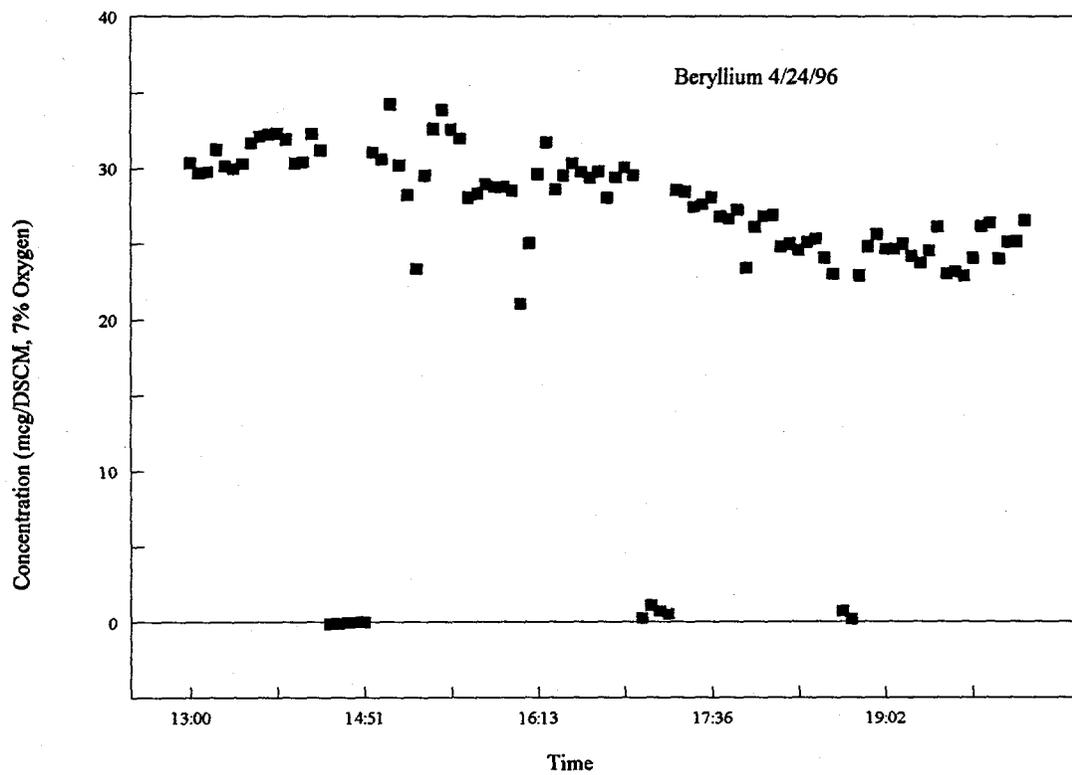


Figure 3. Beryllium data from 4/24 illustrating rapid response time of Navy/TJA CEM.

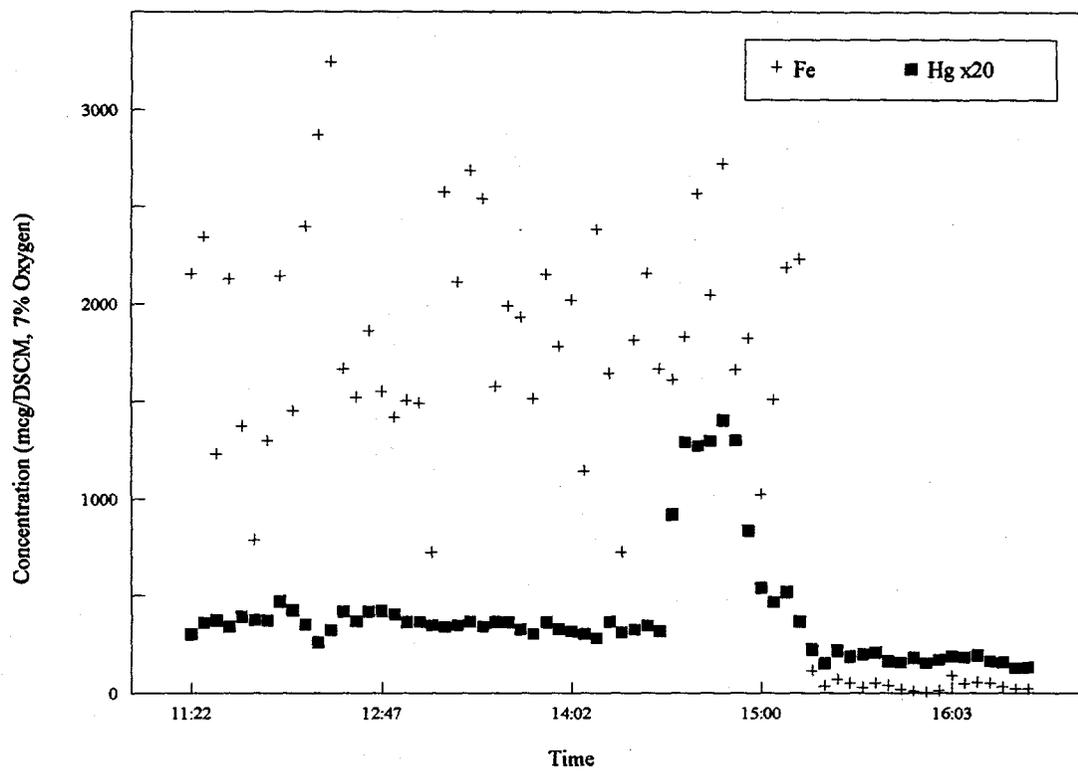


Figure 6. Superimposed mercury and iron data illustrating ability of Navy/TJA CEM to account for and subtract iron spectral interference from mercury determination.

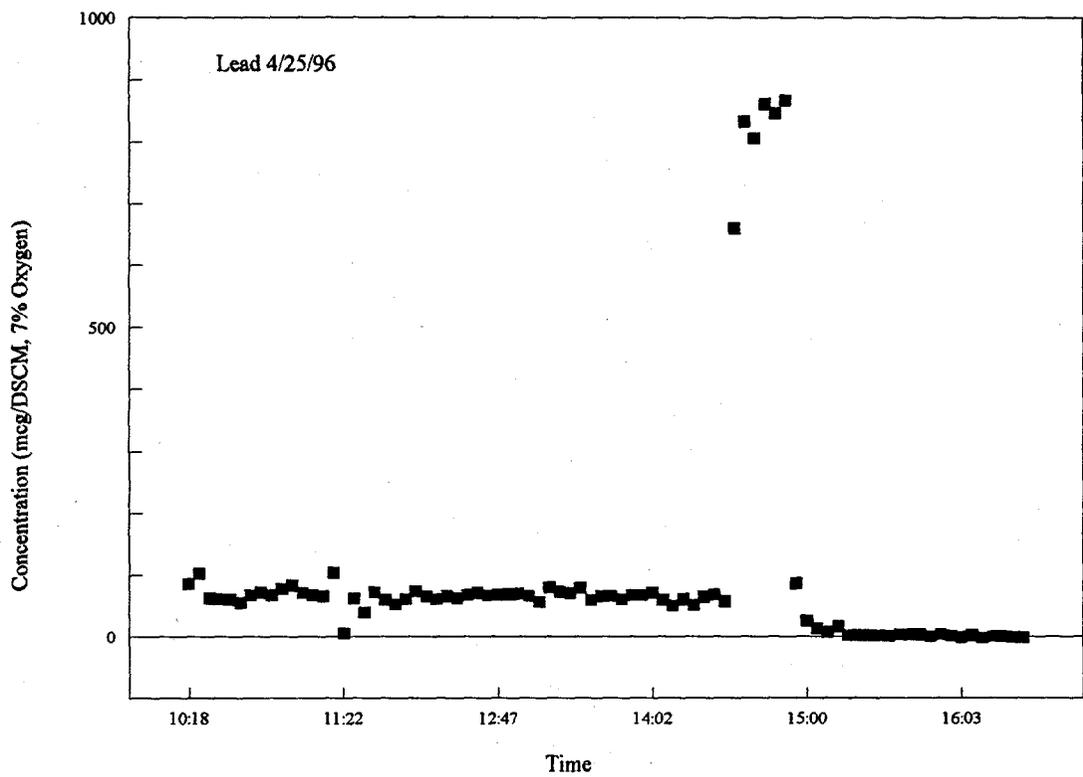


Figure 7. Lead data from 4/25 illustrating Navy/TJA CEM response to ten-fold increase in metal loading of effluent followed by extinction of metal introduction.

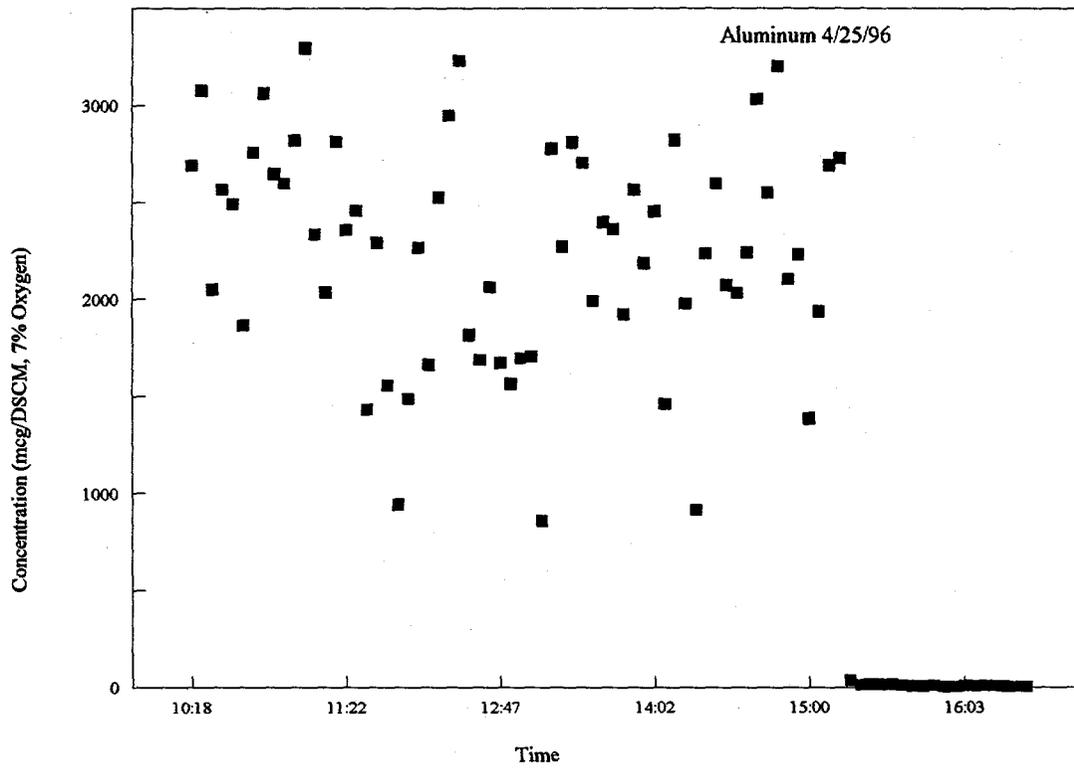


Figure 9. Aluminum data from 4/25/96. Aluminum is a major component of fly ash.

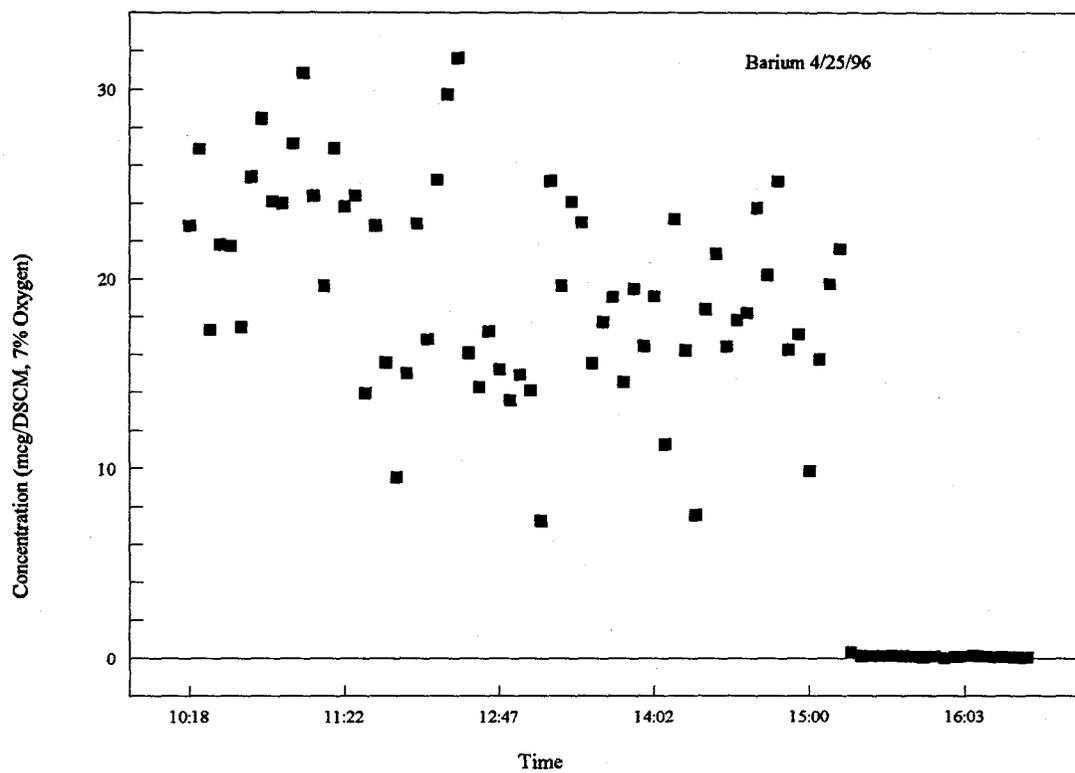


Figure 10. Barium data from 4/25/96. Barium is a minor component of fly ash.

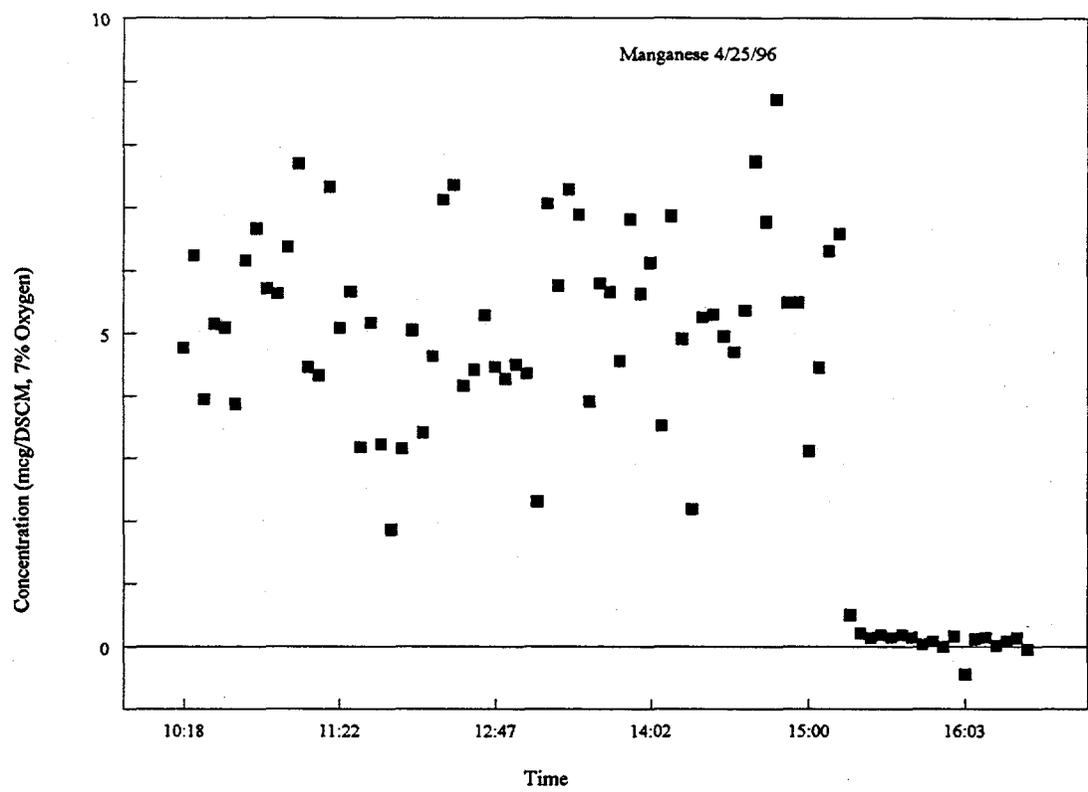


Figure 11. Manganese data from 4/25/96. Manganese is a minor component of fly ash.

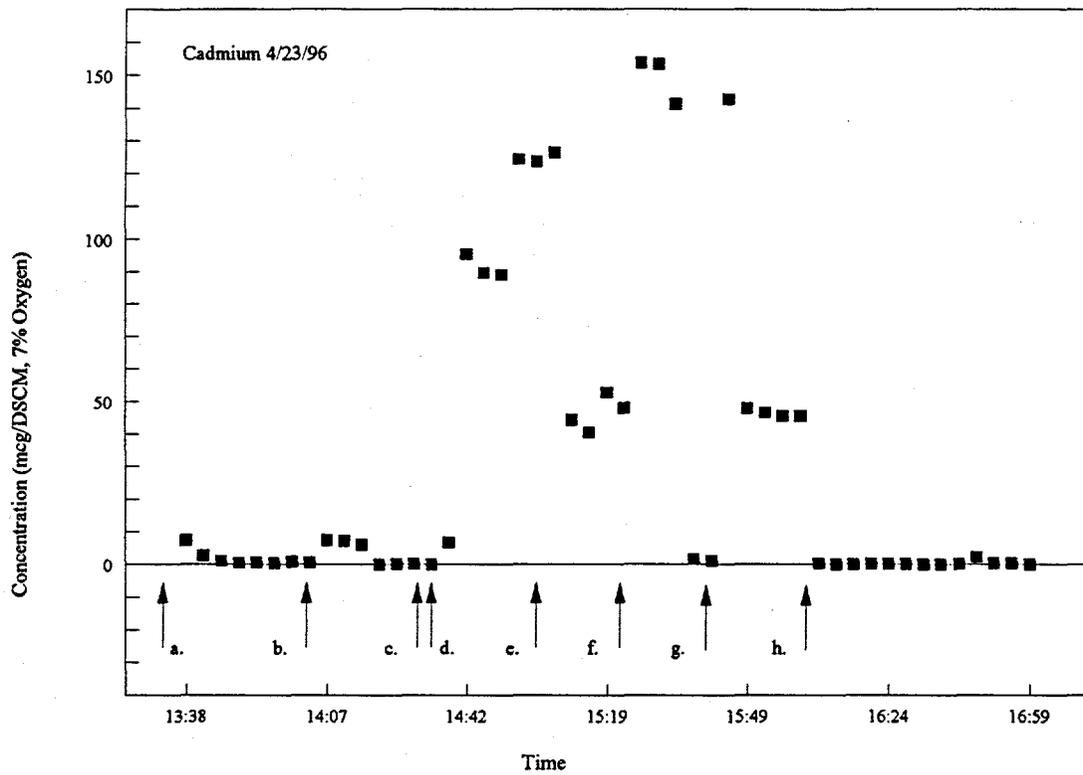


Figure 12. Cadmium data from 4/23 illustrating response to feed switching. Events are as follows: a. DI water start; b. HNO₃ start; c. HNO₃ stop; d. medium metals start, e. switch to low metals, f. switch to medium metals, start fly ash, g. switch to low metals, h. stop metals feed, stop fly ash. Event timing is approximate.

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APPENDIX F

FINAL REPORT OF SNL CEM DEVELOPER TEAM

Field Tests of a Continuous Emissions Monitor for Metals Based on Laser Spark Spectroscopy

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Abstract

Sandia National Laboratories performed field tests of a prototype advanced continuous metal emissions monitor at the U.S. Environmental Protection Agency's Rotary Kiln Incinerator Simulator (RKIS) at Research Triangle Park, North Carolina, during April, 1996. The prototype metals monitor is based on laser-spark spectroscopy and has capabilities to provide on-line determination of metals concentration as well as to provide facility operators with an indication of hazardous metals emissions levels relative to emissions limits. The laser-spark monitor was operated remotely from a location approximately 10 meters from the measurement position. In these tests, the CEM monitored emissions from the RKIS while known quantities of arsenic, antimony, beryllium, cadmium, chromium, lead, and mercury were added to the flow. Information on the metals content of the exhaust flow was determined both by analyzing averages of the signal derived from multiple laser pulses, as well as by processing the signal from a sequence of individual laser pulses on a shot-by-shot basis. The Sandia laser-spark monitor measured beryllium, cadmium, chromium, and lead in real time at concentrations that are close to reported detection limits determined in the laboratory. These measurements relied on an *automated* procedure to acquire and analyze average spectra from multiple laser shots. Concentrations determined using the laser-spark monitor will later be compared with concentrations determined by standard reference methods that rely on collecting and analyzing a portion of the exhaust-duct flow.

Field Tests of a Continuous Emissions Monitor for Metals Based on Laser Spark Spectroscopy

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I. Introduction

A major challenge in gaining approval for thermal waste treatment plants is convincing the public and regulators that the effluent from the treatment process is free from toxic compounds. Metals, in particular, can be highly toxic even in small amounts and are among the most serious health risks of any emissions from thermal treatment facilities. Continuous monitoring of these metals in the waste-treatment effluent could provide assurance that public health and safety is not endangered, but suitable monitors are not currently available.

The U.S. Department of Energy has sponsored a project at Sandia National Laboratories to develop and demonstrate an advanced emissions monitor that will continuously monitor metal emissions in offgas from thermal treatment units. This effort has led to the development of a prototype metals monitor based on an optical technique known as laser-spark spectroscopy (also referred to as *Laser-Induced-Breakdown Spectroscopy*, or *LIBS*). Reported here are field tests of the prototype laser-spark monitor that were conducted on the Rotary Kiln Incinerator Simulator (RKIS) located at the U.S. Environmental Protection Agency facility in Research Triangle Park, NC. The overall objective of the tests was to evaluate the ability of the laser-spark metals monitor (as well as other advanced metals monitors currently being developed) to operate continuously and reliably in a field environment while providing real-time measurements of metal emissions. Our specific technical goals include: (a) demonstrating that regulated metals can be measured at concentrations comparable to regulated limits; (b) comparing metals measurements obtained using the laser-spark monitor to results obtained using standard reference methods; and (c) evaluating the ability of the laser-spark monitor to follow transient variations in metal concentrations that result from temporal variations in operating parameters or flow conditions. A secondary objective was to obtain performance information that can be used to make engineering improvements in the prototype monitor and the associated operating procedures.

II. Technology Description

Laser spark spectroscopy

In laser spark spectroscopy, a high-energy pulsed laser is focused in the effluent stream. The high energy density in the focal region generates an optical breakdown (a laser-induced plasma, or "laser spark") in which particles and molecules are decomposed into excited atoms and ions. The variation of the intensity of light emitted by these excited species as a function of wavelength (the "spectral signature" of the emitting species)

correlates directly with the type and quantity of metal present. Thus, measurements of this optical emission can be used to monitor the concentration of toxic metals in the effluent stream. An obvious advantage of a laser-spark-based continuous emissions monitor (CEM) is the inherent ability of the technique to measure atomic species embedded in either particles, fine aerosols, or vapors *in-situ* in a stack. The laser-spark technology is very promising for measuring metals in the effluent from hazardous waste treatment units, as well as for other applications, including monitoring metal emissions from munitions deactivation furnaces, fossil power plants, industrial furnaces and boilers, and industrial processes such as electroplating.

Prototype Laser-Spark CEM

The prototype laser-spark metals monitor developed at Sandia consists of four basic pieces: (1) an optical probe, which contains a pulsed Nd:YAG laser plus focusing and collection optics; (2) an instrumentation rack that contains control instrumentation; (3) a rack that holds the laser power supply, a spectrometer, and a CCD detector; and (4) a rack that holds two personal computers for data acquisition, data analysis, and experimental control. Individual subsystems are described below. The complete prototype is rugged, easily transported, and easily installed at a waste treatment facility. The monitor requires only a single port for optical access to the stack, an important advantage since, in many applications, suitable ports may be few and not easily changed. The distance from the probe hardware to the measurement volume is adjustable, and the monitor requires only minimal optical alignment, which is easily performed in the field.

Optical probe

The configuration of the optical probe assembly is shown in Figure 1. The Q-switched, laser output at 1064 nm is expanded and collimated by a pair of lenses, passes through a hole in a mirror that is mounted at 45 degrees relative to the beam, and then is focused in the effluent stream by a plano-convex lens. The laser-focusing lens also serves to collect and collimate a portion of the optical emission from the laser-induced breakdown. Most of this collected emission reflects off the mirror through which the incident laser beam originally passed, effectively separating the collected plasma emission from the counter-propagating laser beam. This emission then reflects off a second mirror and is focused on the tip of a 3-meter-long fiber-optic bundle, which transmits the plasma emission to the instrumentation-rack-mounted spectrometer and detector.

Instrumentation modules

Three separate assemblies house the spectrometer, detector, electronics, power supplies, and computers. Individual instruments are mounted in steel-framed instrument racks that are connected by rubber shock-absorbing mounts to rugged, injection-molded-plastic, containment shells. The instrumentation modules are sufficiently shock-protective that a separate external shipping container is not required.

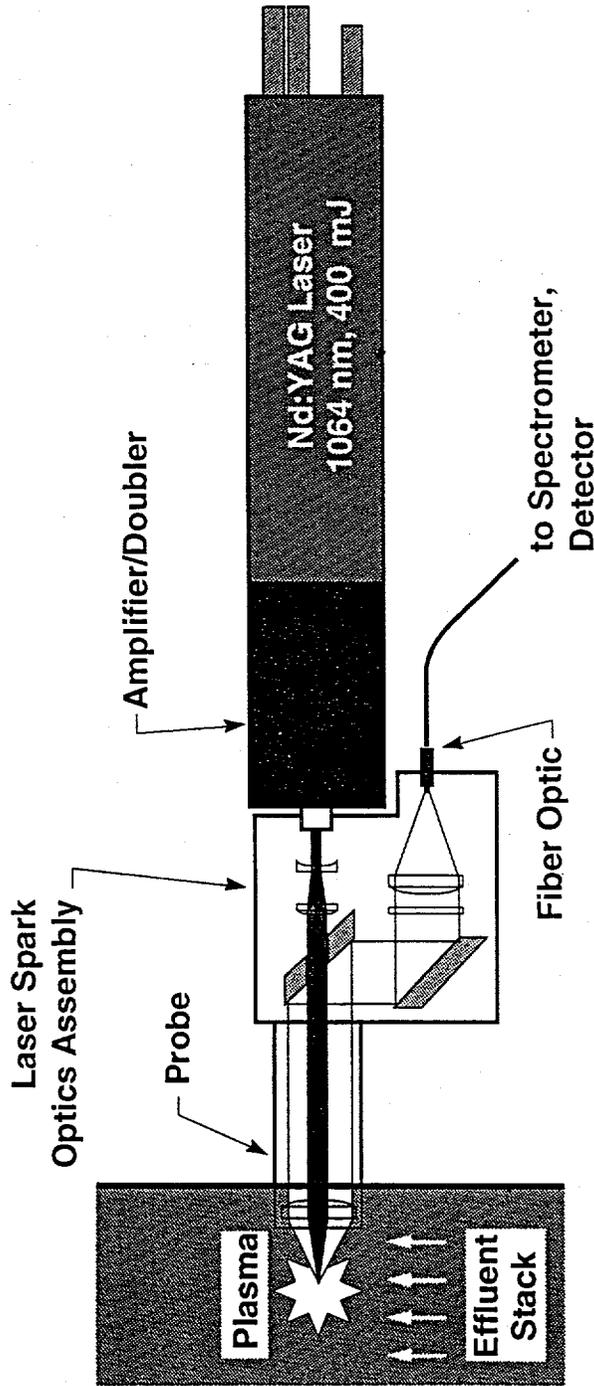


Figure 1. Optical layout of laser-spark metal-emissions monitor.

External connections

The only electrical connections required for the complete monitor system are a 110-V line for the uninterruptable power supply (UPS) and a 208-V, single-phase line for the laser power supply. All other electrical devices are plugged into the UPS. In the tests described here, a large liquid-nitrogen dewar was used to supply small gas flows to purge optical components. A closed-cycle cooler provided slightly chilled water to cool the detector array.

Characterization of monitor response

We characterized the response of the prototype metal-emissions monitor by conducting laboratory experiments on well-characterized flows. In these tests, a fine mist of a metal solution was dispersed by a nebulizer positioned directly below the probe focal volume. For each test metal, we scanned the laser-spark emission spectrum to determine the strongest emission features for individual metals and to identify potential interferences between emission from different species. Single-metal survey spectra displayed one or more distinct optical emission lines for each of the metals that were examined. Individual lines were identified using standard tabulations of atomic emission spectra. In the cases where more than one metal emitted light at a particular wavelength, we sought alternate emission lines that were interference-free.

Similar experiments were performed previously to determine the minimum detectable concentration for each of the toxic metals introduced in these field tests. Here we define the minimum detectable concentration for each metal as the metal concentration for which the ratio of the peak line intensity to the noise in the underlying background has a value of 3. The minimum detectable concentrations for the seven metals examined in the EPA RKIS tests are listed in Table I. For mercury, detection limits are specified for two different detection wavelengths. In practice, detection of mercury emission at 253.7 nm may not be feasible, since emission from this transition (which terminates in the ground state) will be absorbed by ground-state mercury vapor in the surrounding gases. For typical optical path lengths in stack gases, the true mercury detection limit will be the higher value corresponding to the 365.0-nm line.

Table I. Minimum detectable concentrations of the seven metals targeted in the EPA RKIS field tests, based on laboratory measurements

Element (and detection wavelength)	Minimum Detectable Concentration ($\mu\text{g}/\text{acm}$)
Be (313.1 nm)	2
Cd (226.5 nm)	20
Cr (283.6 nm)	30
Pb (220.4 nm)	200
Sb (259.8 nm)	250
As (228.8 nm)	450
Hg (365.0 nm)	900
Hg (253.7 nm)	250

III. CEM Operation

In these tests, one important benefit for the CEM developers was the opportunity for evaluation of different operating procedures and analysis techniques and for identify areas where future work can will lead to additional improvements in the measurement system. At the same time, it is important to benchmark how well metal concentrations determined using by the CEMs in their present form compare to measurements derived using established extractive-sampling techniques. In its current state of development, the Sandia laser-spark monitor determines metal concentrations continuously and in real time by analyzing the average emission spectra determined from multiple laser pulses. The bulk of the present section will describe our standard procedure for acquiring and analyzing spectra obtained from multiple-laser-shot averages. Alternative methods for analyzing the information contained in the multiple-shot averages, as well as methods of acquiring and analyzing sequences of individual single-shot spectra, will be the subject of a later paper. Conditional analysis of sequences of single-shot spectra will be discussed only briefly in this report.

Data acquisition and analysis procedures for multiple-laser-shot averages

The Sandia CEM software is composed of two major program components, one for data acquisition and the other for data analysis, that function as an integrated unit. These programs share common modules for transferring data between them. Scanning and averaging parameters, as well as some instrument settings, are user-set from the data acquisition control panel. Spectra can be acquired as a single scan of the CCD array, or as an average of multiple CCD-array scans. Acquired spectra are averaged and displayed on the control panel in real time. In addition, the programs contain capabilities for generating, editing, plotting, and printing data files and for exporting data to third-party software packages.

Once a spectrum is acquired, analysis of this data to determine metal concentrations begins automatically, even as the data-acquisition computer starts to acquire additional spectra. Our analysis procedure for determining metal concentrations from laser-spark measurements relies on fitting to the stack spectral measurements a set of single-metal reference spectra. These single-metal reference spectra are obtained prior to the field measurements by measuring the response to known concentrations of individual metals. In the field, a numerical fitting algorithm performs a two-parameter fit to determine the linear combination of the reference spectrum and a "background" spectrum (measured with no metal present) that best fits the spectrum measured in the stack flow. The best-fit scaling factor for the reference spectrum is then used to determine the metal concentration in the stack. That is, the stack metal concentration is equal to the product of the metal concentration used to generate the reference spectrum times the best-fit scaling factor. (In some cases, stack measurements were made using a different number of CCD pixel rows than were used for generating the reference spectra – in these cases, the scaling factor was also multiplied by an experimentally determined factor that compensates for the different effective detector area.) The numerical fitting procedure also determines a correlation parameter that indicates the goodness of the fit of the reference spectrum to the field measurements. If the correlation parameter is less than 0.5, the fit is judged to be not good enough to indicate a valid measurement.

Field calibration procedure

Implementation of a suitable field calibration procedure for the laser-spark-spectroscopy-based metal emissions monitor is important for gaining acceptance of laser-spark metals measurements by regulators and by the public. The fundamental purpose of the calibration procedure should be to determine as accurately as possible the response of the monitoring device to a known metal concentration under actual field conditions in a way that accounts for changes in instrument performance. The calibration procedure that was planned for the EPA RKIS tests is to measure the response of the monitor to known concentrations of metal produced at the time of the tests by a portable aerosol generator. For this purpose, we used a pneumatic nebulizer identical to that incorporated in commercial Inductively Coupled Plasma Atomic Emission Spectrometers, which produced a flow containing 10 ppm of the metal that was introduced to the nebulizer. The nebulizer was enclosed in a separate cell that mated to the input/output optics of the laser-spark metal emissions monitor. Thus, the response of the complete metal-emissions monitor to the known metal concentration was determined. These reference measurements serve as the instrument calibration, determining system response for subsequent measurements in the actual stack flow.

At the present time, it is necessary to remove the metal emissions monitor completely from its coupling with the stack in order to insert the calibration cell. (A modified design in which the calibration cell is mounted permanently between the metal-emissions monitor and the stack is currently being fabricated. For this configuration, the monitor can be recalibrated without removal from the stack.) Limited space at the location where the Sandia laser-spark monitor was mounted for the EPA RKIS tests prevented the probe from being retracted sufficiently far to insert the calibration cell. An initial calibration was performed prior to installation of the monitor, but it was not possible to repeat the calibration during the test series.

Zero-check procedure

The instrument zero is checked by measuring complete optical emission spectra in the flow duct prior to the addition of waste and then analyzing the measurements for concentrations of all fourteen target metals. This determines the instrument response for zero metal concentration.

Spectral calibration procedure

The correspondence between wavelength and CCD detector element can shift due to changes in temperature or due to mechanical effects. Spectral calibrations are used to determine the wavelengths corresponding to individual detector elements for a specified spectrometer grating position. Such calibrations are performed by measuring the emission spectrum from a mercury discharge lamp for each grating position that was used during CEM data acquisition. The measured discharge lamp spectra are then be used to assign absolute wavelengths to detector elements corresponding to known mercury-emission wavelengths.

Similar mercury discharge lamp spectra are measured immediately prior to the measurement of calibration reference spectra used for quantitative analysis of metal emission measurements; these discharge-lamp spectra were used in the same manner to determine the wavelength scales for the reference spectra.

Daily test sequence

The *planned* basic sequence of events for each test day is summarized below:

1. Perform a spectral calibration to determine the wavelengths corresponding to individual detector elements for different spectrometer settings.
2. Calibrate the response of the system to aerosols containing known concentrations of metals. In practice, repeated calibrations on each test day were not possible because a ventilation duct interfered with retracting the probe.
3. Check the instrument zero by performing one or more complete spectral scans in the flow duct before the addition of waste. Measured spectra were analyzed to determine the apparent concentrations for all target metals.
4. Perform repeated survey spectral scans at varying averaging times throughout the day, and make repeated measurements in selected wavelength regions.
5. At the end of the day, perform a final zero check with metal feed off.
6. At the end of the day, and at intermediate times as necessary, install the calibration aerosol source and perform a response (calibration) check. Again, repeated calibrations were not possible because of interferences with movement of the probe.

IV. Field Experiments

Installation of the prototype CEM

Upon arrival at the EPA RKIS facility, three Sandia personnel installed the prototype CEM at an access port located on a horizontal duct that contained the effluent stream from the rotary kiln incinerator. The entire installation required less than two days, including time required for uncrating instruments, checking for damage (none was apparent), assembling the probe support structure, establishing electrical and water connections, and performing a field calibration of the monitor. No realignment of the probe optical components was performed in the field. The field calibration showed that the response of the metals monitor to each of the target metals (Table I) remained within five to ten percent of that measured prior to shipping. Calibration reference spectra measured in the laboratory prior to shipping were used throughout the EPA tests. Spectral calibrations were repeated daily.

The extension of the probe containing the laser-focusing and emission-collection lens passed through an O-ring seal that was attached to a standard flange on the duct. In principle, this arrangement permits the measurement location in the duct to be translated to any position on the duct diameter simply by sliding the complete optical probe on its support stand. However, since the test organizers requested that the physical probe not protrude into the interior of the duct, the probe position was held fixed such that the end of the probe was even with the interior wall of the duct. This arrangement places the measurement volume (the spark location) approximately 7.5 cm from the near wall of the duct (2.5 cm from the duct centerline).

A small flow of gaseous nitrogen (provided by the boil-off from a liquid nitrogen dewar) was directed inward across the face of the focusing/collection lens to help keep the surface clean. The lens was examined and cleaned at the end of each test day. This purge system was found to work very well for keeping the lens relatively free of particulate deposits.

Test conditions and anticipated results

Tests were scheduled for Monday, Wednesday, and Friday during the week of April 22, with Tuesday and Thursday set aside for optional checkout tests to be performed by the CEM technology developers. On each of the scheduled primary test days, three to five defined reference-method (RM) periods of nominally 1-2 hours duration were dedicated to collecting physical samples of the duct flow for analysis using standard batch analysis techniques. Nominal conditions for the demonstration tests are summarized in the Quality Assurance Project Plan prepared by Acurex Environmental Corporation. Before the test series, facility personnel prepared three metal solutions that were to be introduced to the flow on three separate test days during the demonstration program. Target flue gas concentrations of antimony, arsenic, beryllium, cadmium, chromium, and lead were roughly 60 $\mu\text{g}/\text{dscm}$ on Monday, 15 $\mu\text{g}/\text{dscm}$ on Wednesday, and 600 $\mu\text{g}/\text{dscm}$ on Friday. Target mercury concentrations were 100, 25, and 1000 $\mu\text{g}/\text{dscm}$ on Monday, Wednesday, and Friday, respectively. During the test week, it was decided to repeat the Monday test conditions (intermediate concentration levels) on Thursday.

Based on the minimum detectable concentrations listed in Table I, we anticipated that we should be able to detect beryllium at the "low" target concentration; beryllium, cadmium, and chromium at the "intermediate" level; and all species at the "high" level – presuming in all cases that the target metal concentrations were attained.

CEM operating parameters

During each RM period, we attempted to obtain real-time measurements for each of the seven toxic metals by acquiring and analyzing sets of multiple-laser-shot average spectra at a sequence of spectrometer settings that were chosen so that emission at each of the detection wavelengths listed in Table I (plus a number of secondary emission lines) was measured for at least one spectrometer setting. In these multiple-shot experiments, the laser flashlamp was pumped at a rate of 5 Hz, but the cavity Q-switch was only triggered on alternate flashlamp firings, so that pulsed laser output was obtained at a 2.5-Hz pulse repetition rate. The single-pulse laser energy at 1.06 μm was approximately 600 mJ. For each set point, emission measurements were typically averaged over either 25 or 100 consecutive laser pulses (in either a 10- or 40-second period). Operation in this averaging mode enhances the signal-to-noise ratio if all shots are roughly the same and also reduces the disk space required for storing data. We measured laser-spark emission spectra at varying averaging times throughout each test day. Normally, we started by obtaining a complete spectral survey of spark emission in the spectral region from 215 nm to 320 nm. This was accomplished by acquiring average emission spectra for an overlapping sequence of 30-nm-wide spectral bands that spanned this spectral region. We then performed repeated measurements for specific wavelength regions where we were most likely to detect optical emission from target metals.

During most RM periods, we also acquired and saved for later analysis sequences of single-laser-pulse spectra acquired from 50 to 100 consecutive individual laser pulses. For

these tests, we pulsed the laser flashlamps at a repetition rate of 6 Hz and triggered the Q-switch on every flashlamp firing so that laser output was also obtained at a 6-Hz repetition rate. This is the maximum rate at which the data acquisition system as presently configured can acquire spectra from the CCD detector. Operation in this single-shot mode offers the potential for enhanced signal-to-noise ratios if metal-containing particles are "hit" on only a portion of the laser pulses and if we conditionally analyze only those spectra that correspond to "hits" on these particles. The disadvantage of this type of measurement is that great amounts of disk space are required to save the many individual spectra, and we do not *currently* have the capability to analyze these spectra in real time (although this should ultimately be possible).

Performance of CEM hardware and data-acquisition systems

The monitor hardware operated reliably with no equipment failures throughout the duration of the tests. Laser power remained stable within a few percent for each complete test day. No alignment of the probe optics or adjustment of the laser was performed either upon arrival at the test facility or at any time during the test week.

The only major problem encountered with the data-acquisition system was a breakdown in the optical GPIB link between the data acquisition computer and the CCD controller. We experienced this difficulty at the start of the first test day, and, as a result, we were unable to acquire averaged spectra during the first two RM periods as we worked to identify the problem. Normal operations were resumed for the third RM period and continued for the duration of the test week.

Spectral calibrations

We found that emission-line positions shifted by no more than 1 or 2 CCD pixels during the course of the tests. Since the shifts were so small, updated spectral calibrations were incorporated in the data analysis program only a couple of times during the test week, when we noticed *slight* worsening of the correlation coefficient that characterizes the goodness of the data fitting.

Zero checks

The data-fitting procedure determined no significant correlations (non-zero concentration) for the target metals prior to the first addition of metals in the morning or after metals had been turned off for 20 to 30 minutes at the end of the day. We performed the zero check both in the morning and evening early in the week, but only checked occasionally later in the test week.

Reported metals measurements

Measurements of beryllium, cadmium, chromium, and lead were determined in real time from multi-laser-shot average spectra throughout the test week, although not all of the metals could be determined for all test conditions. Disk files containing the metal concentrations determined for these species were submitted to the organizing committee after each test day. We reported only those measurements that we were able to perform repeatedly. That is, we included only those measurements for which the data-analysis procedure repeatedly provided statistically valid fits of single-metal reference spectra to the data. If the data showed only isolated or sporadic measurements of a given metal in a given spectral band, then those measurements were rejected. A few of the concentrations that

were reported early in the week were determined later to be spurious, resulting from fits to interfering species or to noise features – a revised set of measured concentrations that had been screened for such spurious fits was submitted on a single data disk at the end of the test week. These measurements form the basis for the metal concentrations that are reported for each reference method period in the following section. A few additional measurements have been discarded in this analysis, but, otherwise, only relatively minor adjustments were made to the numerical values reported during the test week, as explained in the following section.

Raw spectral measurements, including those that had not yet been processed at the conclusion of the test week, were not requested nor submitted. These include: (1) multi-shot average spectra for which significant fits were not determined by the automated analysis procedure but which will be further analyzed interactively or through use of alternate analysis techniques; and (2) sequences of single-laser-shot emission spectra that will be conditionally analyzed to determine metal concentrations.

V. Results

Measurements for RM periods: real-time results from multi-shot averages

Laser-spark metal-concentration measurements determined in real time from multi-shot averages are reported here for all RM periods during the week except for RM1 and RM2 on Monday (intermediate metal concentration level) and RM3 on Thursday (also at the intermediate metal concentration level). The gap for the first two RM periods was due to a system lockup that halted communications between the data-acquisition and data-analysis computers. (We were still able to acquire sequences of single-laser-shot emission spectra during this period; inferred metal concentrations for RM1 and RM2 on Monday will be reported in a future paper.) This difficulty was diagnosed and fixed even as tests continued; real-time analysis for metal concentrations began with RM3. The lack of real-time metals concentrations for RM3 on Thursday also resulted from a communications problem, namely a breakdown in communications between ourselves and the test organizers. Since Thursday was originally scheduled as an optional test day, we were unaware until the conclusion of Thursday that the organizers planned to include measurements for that day in this report. We had made no attempt at real-time measurements during RM3, focusing our efforts instead on acquiring single-shot spectra for later analysis. Again, metal concentrations determined for this period will be reported in a future paper.

For all other RM periods, we determined average metal concentrations during the sampling periods by the method described here. Metal concentrations that were reported at the end of the test week were multiplied by 0.72 to reflect the recent measurement of actual metal concentration emitted by the calibration aerosol source. (Concentrations reported during the RKIS tests were based on the nominal 1% nebulizer efficiency that is stated by the supplier; we reported at the time we submitted our measurements that values would be adjusted once the actual efficiency was measured. Nebulizer output for the calibration conditions was measured May 8-10, 1996 by Insitac Measurement Systems.) We then screened the list of reported measurements to group them according to RM period.

A very few additional measurements were then rejected as being suspect based upon examination of repeated measurements (made using either a second spectral line or by examining the same spectral line at a different spectrometer setting). Although a few cadmium measurements were made using the 214.4-nm line, these measurements did not agree well with the those made at 226.5 nm. Examination of the raw spectra showed that data fits at 214.4 nm were due to a spectral feature that was much smaller than that at 226.5 nm, and, in fact, may have been due to an interfering species or emission irregularity rather than due to cadmium emission. Hence, the measurements at 214.4 nm (215-nm spectrometer setting) were deleted before averaging the cadmium measurements. Similarly, measurements based on the 265.0-nm beryllium line with a spectrometer setting of 280 nm were a factor of about 5 lower than measurements made of the same line with a spectrometer setting of 265 nm and with measurements based on the 313-nm line for two different spectrometer setting. Examination of the raw emission spectra showed that the 214.4-nm line appeared near the very edge of the CCD array (where detector response was varying strongly with position) for the 280-nm spectrometer setting, and these measurements were therefore rejected.

Figures 1 through 13 in the Appendix to this report show all of the multi-shot measurements that were used to determine average concentrations for the individual reference-method periods. Although the general downward trend of concentrations during each test day could reflect a change in calibration, which has not been accounted for here, the trends also could reflect real changes in the rate at which metals were introduced to the system. Detailed comparisons will have to await the release of results obtained from physical sampling. Note that, in fact, there are also several times (notably on April 24) for which the trend of metal concentration within the sampling period is *upward*.

All of the measurements were grouped by metal and by sampling period and were summed directly to determine average values for the RM periods. In some cases, measurements obtained using more than one emission line were averaged together. Average concentrations determined in this way for the individual reference-method periods are summarized in Table II below. Direct comparisons between these results and the measurements obtained using sampling techniques will have to await the release of the sample analysis. However, we can note that (accounting for the conversion between actual cubic meters and dry standard cubic meters) all of the laser-spark measurements reported in Table II are within a factor of 2 to 3 of the target concentration levels for the corresponding RM periods.

We have not yet re-examined those measurements where statistically valid fits were not determined in real time by the automated analysis procedure. For some of these data, we will still be able to determine concentration by manual analysis. In fact, an example where cadmium was determined from a multi-shot average at the "low" concentration level is described in the following section.

Table II. Average Concentration for all Reference-Method Sampling Periods

	Day	Run	Be ($\mu\text{g}/\text{acm}$)	Cd ($\mu\text{g}/\text{acm}$)
1	Mon. 4/22/96	RM1		
2	Mon. 4/22/96	RM2		
3	Mon. 4/22/96	RM3	25.8	71.5
4	Mon. 4/22/96	RM4	18.8	38.7
5	Mon. 4/22/96	RM5	15.4	23.0

	Day	Run	Be ($\mu\text{g}/\text{acm}$)
1	Wed. 4/24/96	RM1	9.90
2	Wed. 4/24/96	RM2	9.24
3	Wed. 4/24/96	RM3	7.93
4	Wed. 4/24/96	RM4	7.66

	Day	Run	Be ($\mu\text{g}/\text{acm}$)	Cd ($\mu\text{g}/\text{acm}$)
1	Thurs. 4/25/96	RM1	21.9	73.5
2	Thurs. 4/25/96	RM2	21.9	64.4

	Day	Run	Be ($\mu\text{g}/\text{acm}$)	Cd ($\mu\text{g}/\text{acm}$)	Cr ($\mu\text{g}/\text{acm}$)	Pb ($\mu\text{g}/\text{acm}$)
1	Fri. 4/26/96	RM1	137	350	71.8	867
2	Fri. 4/26/96	RM2	155	227	73.1	615
3	Fri. 4/26/96	RM3	108	187	49.3	532
4	Fri. 4/26/96	RM4	100	126	49.0	454
5	Fri. 4/26/96	RM5	75.0	133	38.4	439

We were not able to determine concentrations of antimony, arsenic, or mercury from multi-laser-shot average measurements on any of the test days. An emission lines due to cadmium interfered with the strongest arsenic line at 228.8 nm, and there was significant magnesium (which was presented in the flyash) interference with secondary arsenic lines in the vicinity of 280 nm. Detection of antimony also was hindered by the presence of interferences, from iron near the 259.8-nm line and from cadmium near the secondary 226.3-nm line. It is possible that we still will be able to determine antimony and arsenic concentrations from further analysis of the sequences of single-shot spectra obtained during this test series or, in future tests, by detecting these same emission lines with better spectral resolution.

Measurement of mercury for these test conditions is more problematical. The highest target mercury concentration (1000 $\mu\text{g}/\text{dscm}$) is less than the minimum detectable concentration at 365 nm (900 $\mu\text{g}/\text{acm}$ would be roughly 2000 $\mu\text{g}/\text{dscm}$ for typical humid stack flows), so the failure to detect mercury at 365 nm is entirely consistent with the reported detection limits if mercury was indeed present at or below the target concentration. There were no apparent interferences that prevented measurements of the 365-nm line (detection at 253.7 nm was most likely prevented by absorption due to vapor-phase mercury). Analysis of single-shot data would not provide additional information since mercury almost certainly appears in the vapor phase and is present on every laser shot.

Analysis of sequences of individual laser shots

Conditional analysis of sequences of single-laser-shot can result in significantly improved signal-to-noise ratios if a disproportionate amount of the optical emission arises from only a few laser shots. This situation would result if the laser only rarely "hit" particles containing metals or, even if particles were hit frequently, if most of the metals were contained in only a few particles. During the EPA RKIS tests, we acquired a large number of single-shot spectra, which we will analyze in the coming weeks to assess the value of evaluating sequences of single-shot spectra. If conditional analysis of single-shot spectra appears to be useful, this method will in the future be integrated in the data acquisition and analysis software so that single shots can be analyzed in real time to determine metal concentrations. Two sample sets of single-shot measurements are examined here to illustrate the utility of this approach.

We first consider a set of spectra in the vicinity of 230 nm that were measured during the RM2 period on April 24, a test with "low" target concentrations for the toxic metals. Shown in the lower trace of Figure 2a is the average of the spectra obtained on 100 consecutive individual laser shots. First we note that, although the automated data-fitting procedure was not able to determine the cadmium concentration in real time for 100-shot averages on this test day, examination of Figure 2a reveals that the 226.5-nm cadmium peak is indeed barely visible at pixel number 435. Through comparison of this average peak to that obtained during calibration, we determine a cadmium concentration of 16.9 $\mu\text{g}/\text{acm}$. Upon examination of the single-shot spectra that result from individual laser pulses, we observe that the 226.5-nm cadmium peak is much more pronounced in just a few of the spectra than in the others. Figure 2b shows the ratio of the intensity averaged over 3 pixels centered on 226.5 nm to the intensity averaged over 7 pixels in a region far

removed from any line emission features due to cadmium or any other species. The average value of this ratio is about 1.6. Only 5 laser pulses produced spectra for which this ratio was more than 25% above the average value. If we average the spectra for these 5 "greatest hits," we obtain the spectrum shown in the upper trace of Figure 2a. Through analysis of this spectrum, we determine that the average cadmium concentration for these 5 laser shots is 332 $\mu\text{g}/\text{acm}$. If we make the gross assumption that *all* of the cadmium appears in these 5 laser shots (*i.e.*, that the cadmium concentration is zero for all other laser shots), then we determine that the average cadmium concentration over all time is $0.05 \times 332 \mu\text{g}/\text{acm} = 16.6 \mu\text{g}/\text{acm}$ (in close agreement with the value obtained from the 100-shot average). That is, the average cadmium concentration is equal to the average concentration when cadmium is present (332 $\mu\text{g}/\text{acm}$) times the fraction of the time that cadmium is present (5 shots out of 100, or 0.05).

The selection of the criterion that we will analyze only spectra that include cadmium peaks 25% above the average is very arbitrary. We note that if we had chosen in this example to consider instead only peaks that are *double* the average, we would have included only 2 single-shot spectra in our analysis, and we would have determined an average cadmium concentration of 12.4 $\mu\text{g}/\text{acm}$, only 25% less than deduced from including peaks 1.25 times the average. We conclude that conditional analysis of only those spectra that display prominent emission features can provide reasonable estimates of average metal concentrations.

Figures 3a and 3b show a similar example in which conditional analysis of chromium emission features is used to determine the average chromium concentration for a test at intermediate target concentration level (during RM3 on April 25). For this data set, we infer a chromium concentration of 11.4 $\mu\text{g}/\text{acm}$ by analyzing only those spectra for which the emission ratio for the chromium line exceeds the average value by 25%. As in the previous example, the emission ratio only exceeded this value for 5 out of 100 laser shots. This example illustrates one danger of the conditional analysis approach – if we had in this case set the threshold for "hits" to be double the average, we would have concluded that there were no hits containing chromium and, hence, that the average chromium concentration was zero. Nevertheless, we believe that this conditional-analysis approach merits further investigation. We will report additional results in a future paper.

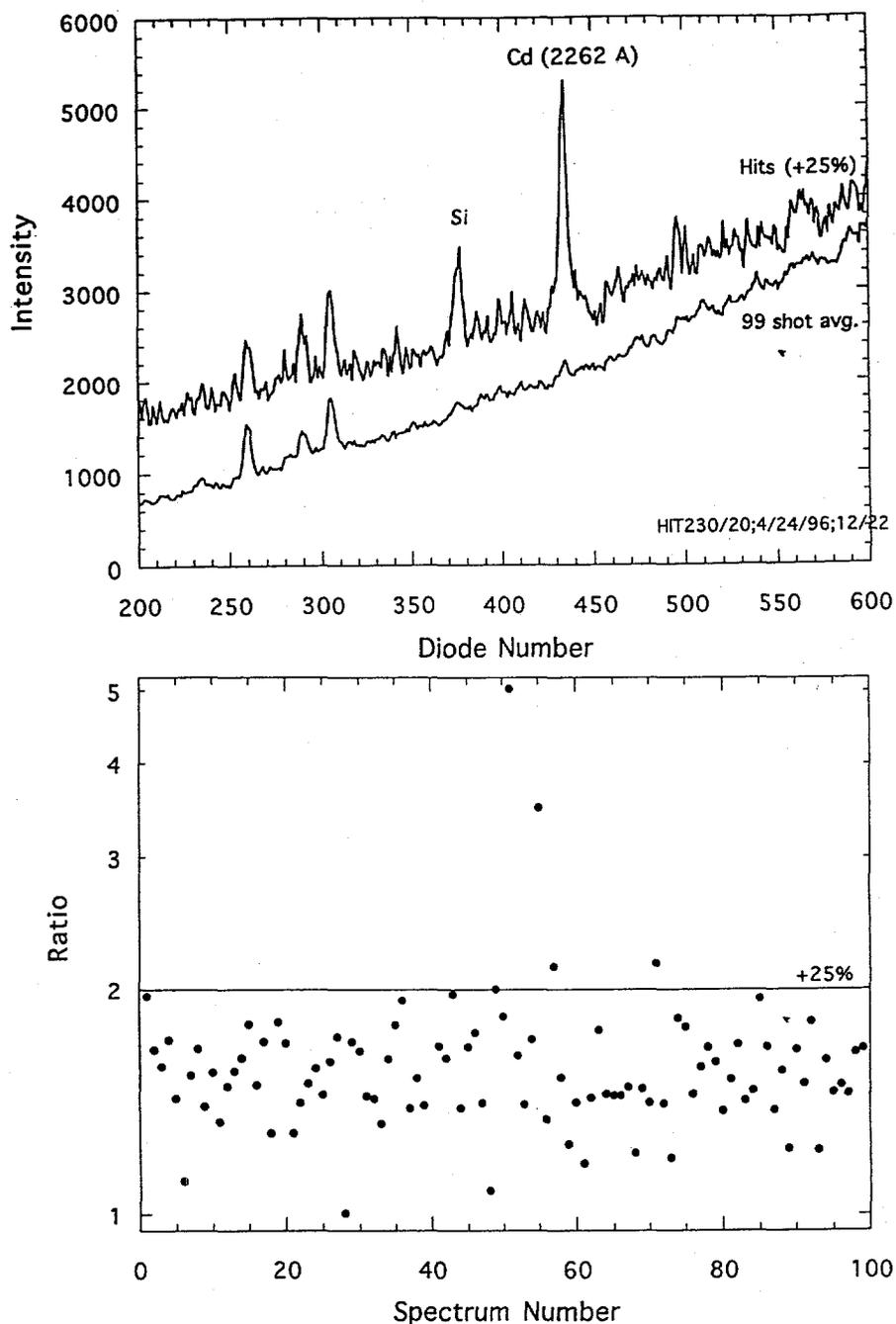


Figure 2. (a) Emission spectra for 230-nm spectrometer setting. Lower trace: average of emission spectra for 100 consecutive laser shots. Upper trace: average of the 5 spectra that display the most prominent peaks at pixel 435, the location of the 226.5-nm cadmium line.

(b) Ratio of intensity at pixel 435 (cadmium emission line) to intensity in a region of the spectrum that is free of discrete emission lines.

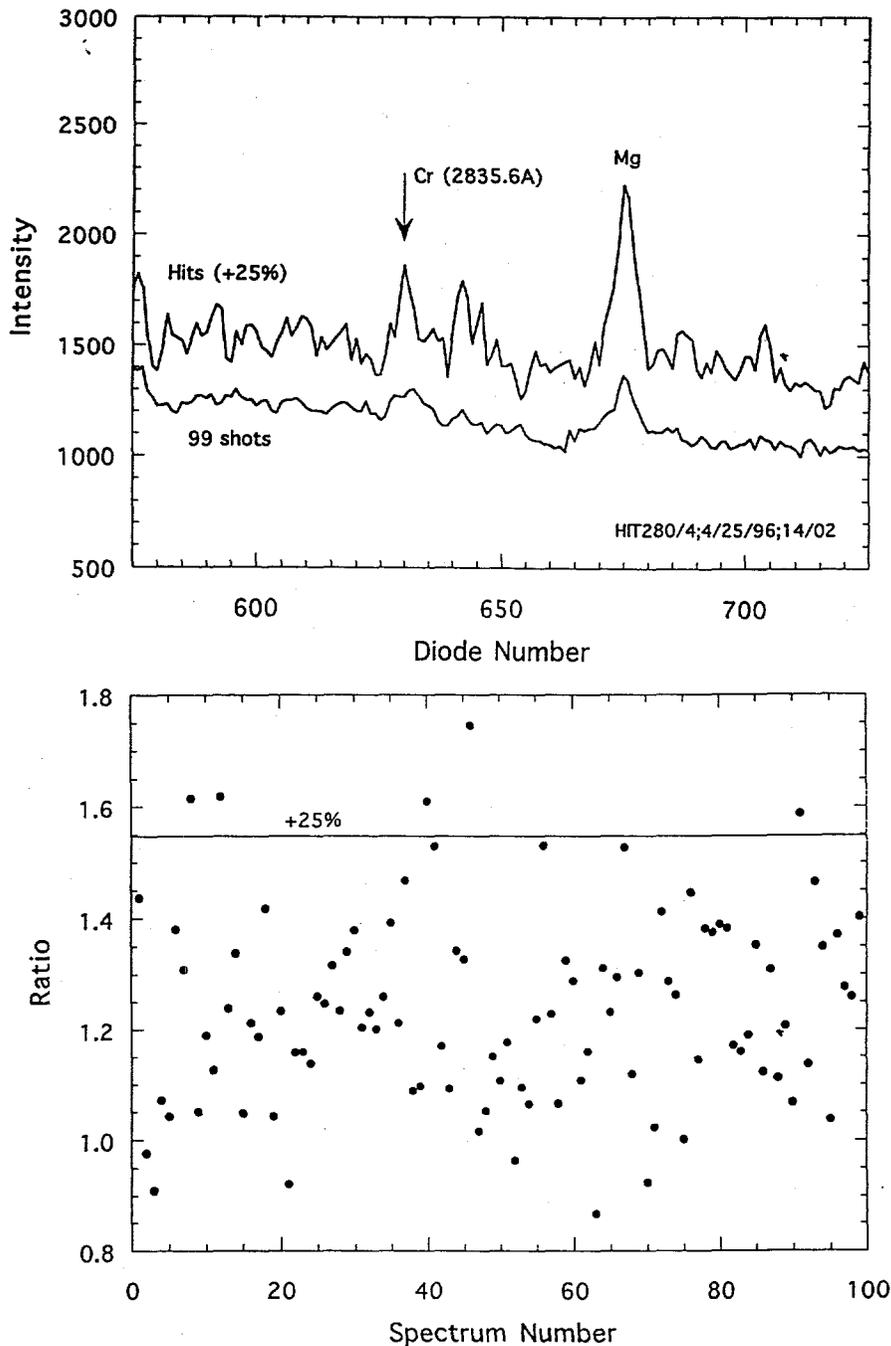


Figure 3. (a) Emission spectra for 280-nm spectrometer setting. Lower trace: average of emission spectra for 100 consecutive laser shots. Upper trace: average of the 5 spectra that display the most prominent peaks at pixel 625, the location of the 283.6-nm chromium line.

(b) Ratio of intensity at pixel 625 (chromium emission line) to intensity in a region of the spectrum that is free of discrete emission lines.

VI. Summary

Reported here are field tests of a continuous emissions monitor for metals that is based on laser spark spectroscopy. Tests were conducted on a rotary kiln incinerator simulator that was operated in a manner so that the effluent simulates that of a full-scale system after exhaust-gas cleanup. These tests demonstrated that the laser-spark technology can be successfully integrated in a well-engineered system that is easy to transport, straightforward to install and operate, and which operates reliably under adverse conditions. Furthermore, the tests demonstrated that the laser-spark monitor can be operated remotely, which will be crucial for future applications to large-scale systems or to systems that present radiological hazards. Most importantly, the tests demonstrated that metal concentrations could be measured in real time by an automated procedure that did not require operator intervention in the analysis of the data.

The Sandia laser-spark monitor measured beryllium, cadmium, chromium, and lead in real time at concentrations that are close to reported detection limits determined in the laboratory. These measurements relied on an *automated* procedure to acquire and analyze average spectra from multiple laser shots. Spectral interferences prevented the measurement of antimony and arsenic by the automated multi-shot procedure, but alternate analysis techniques and improvements in detection spectral resolution may allow these species to be measured in real time with no significant modifications to the current system. In the tests reported here, the monitor was not able to measure mercury, which may in fact have been present at concentrations below the reported detection limit.

We also have demonstrated an off-line technique for the conditional analysis of sequences of individual laser shots, which was used here to determine toxic-metal concentrations at lower levels than was possible using the multi-shot procedure. This technique has the potential for significantly lowering the minimum measurable concentration for species that are present in discrete particles. We are currently doing further work to evaluate and refine this conditional analysis technique, which can be incorporated in the real-time analysis procedure for future tests.

Acknowledgments

Development of the laser-spark CEM was funded by the U.S. DOE Office of Science and Technology Development's Characterization, Monitoring, and Sensors Technology Crosscutting Program (CMST-CP). We would like specifically to thank CMST-CP Program Manager Caroline Purdy for continued support of this program.

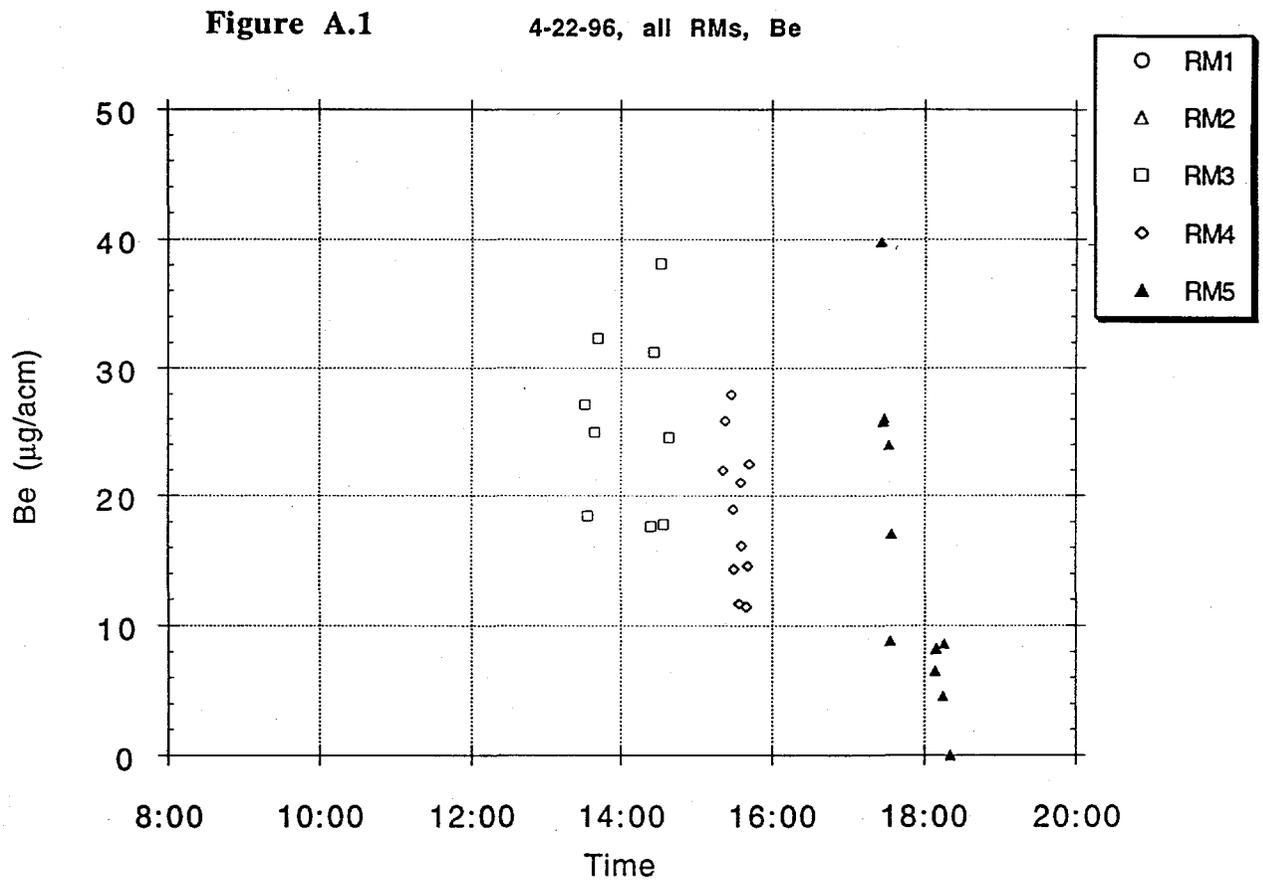
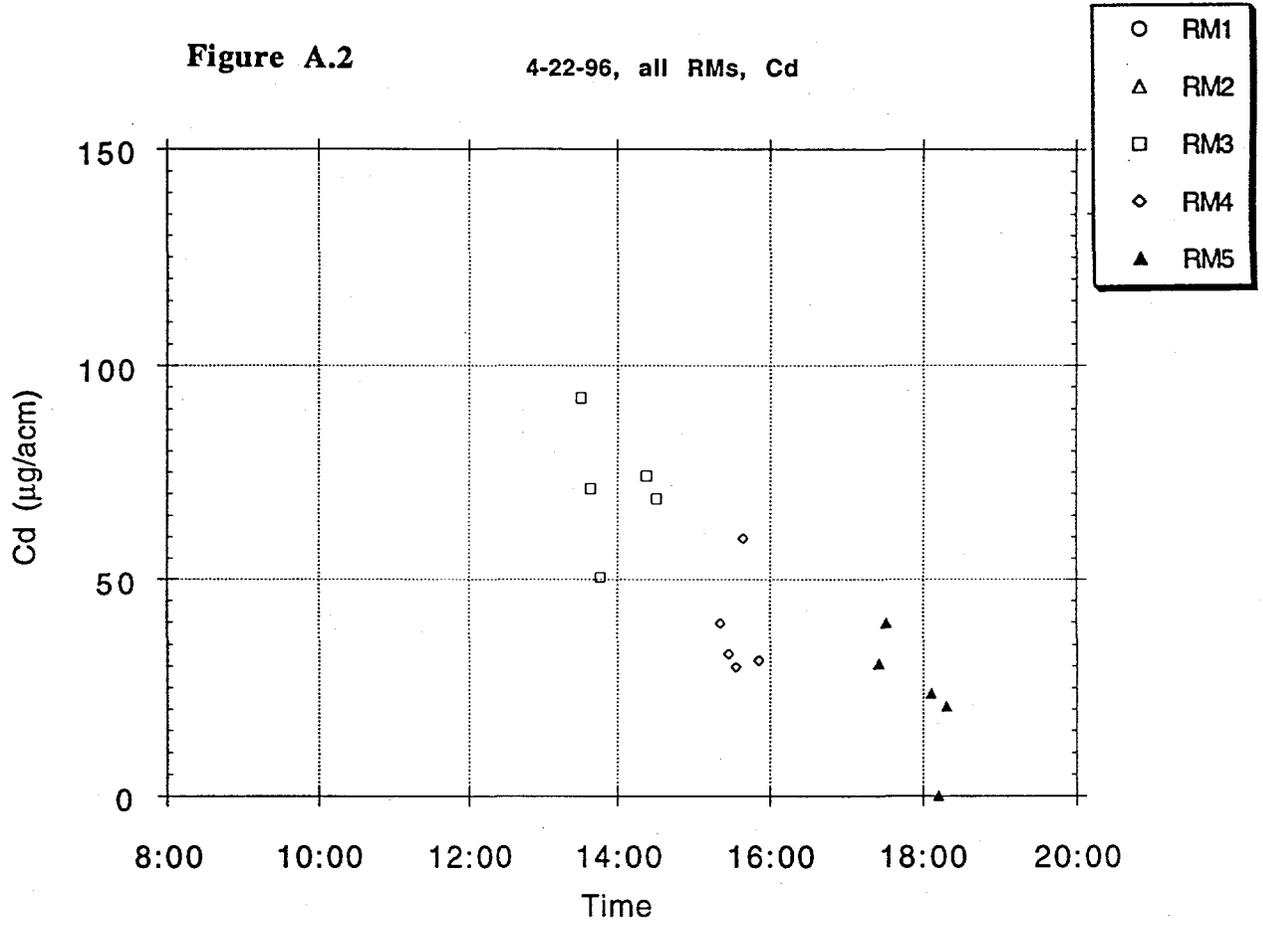
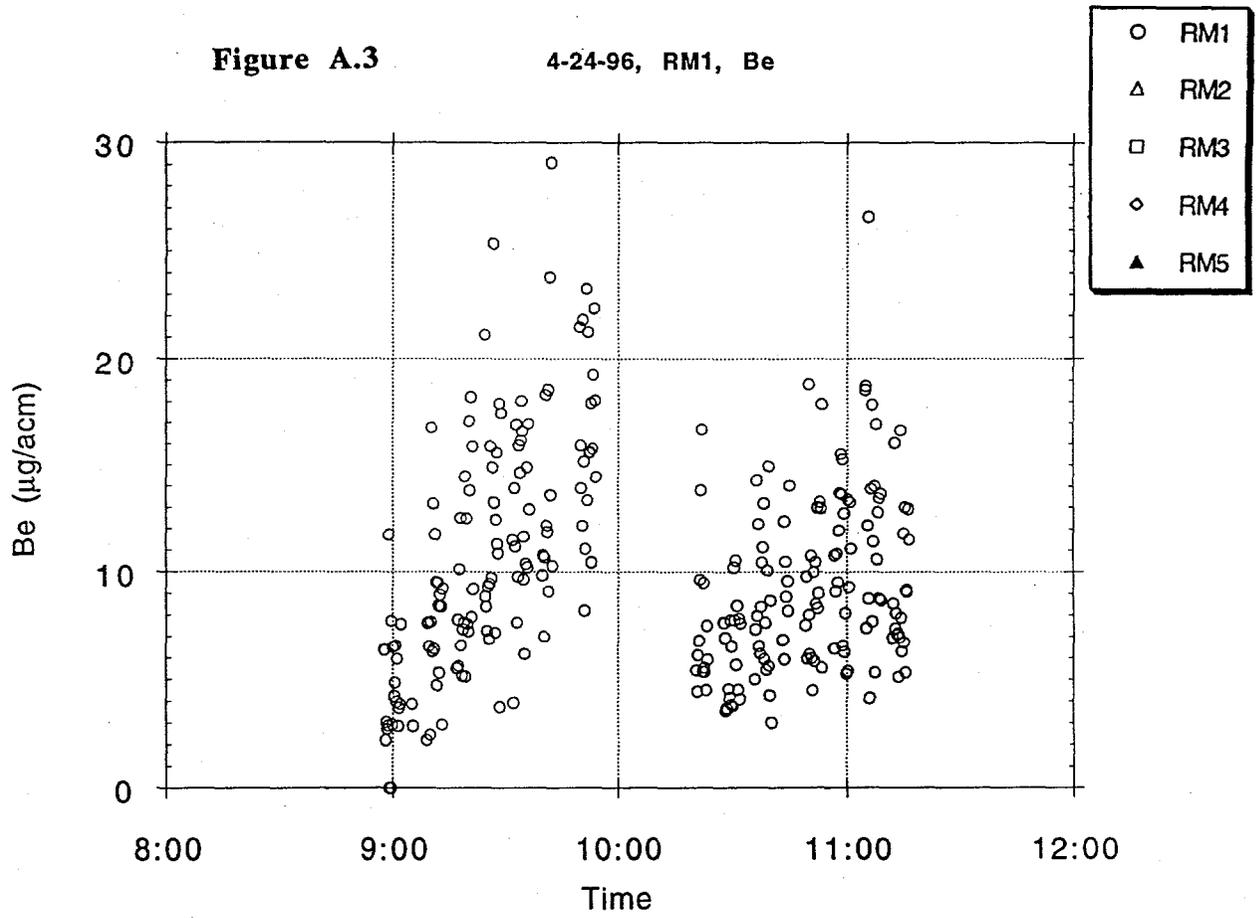
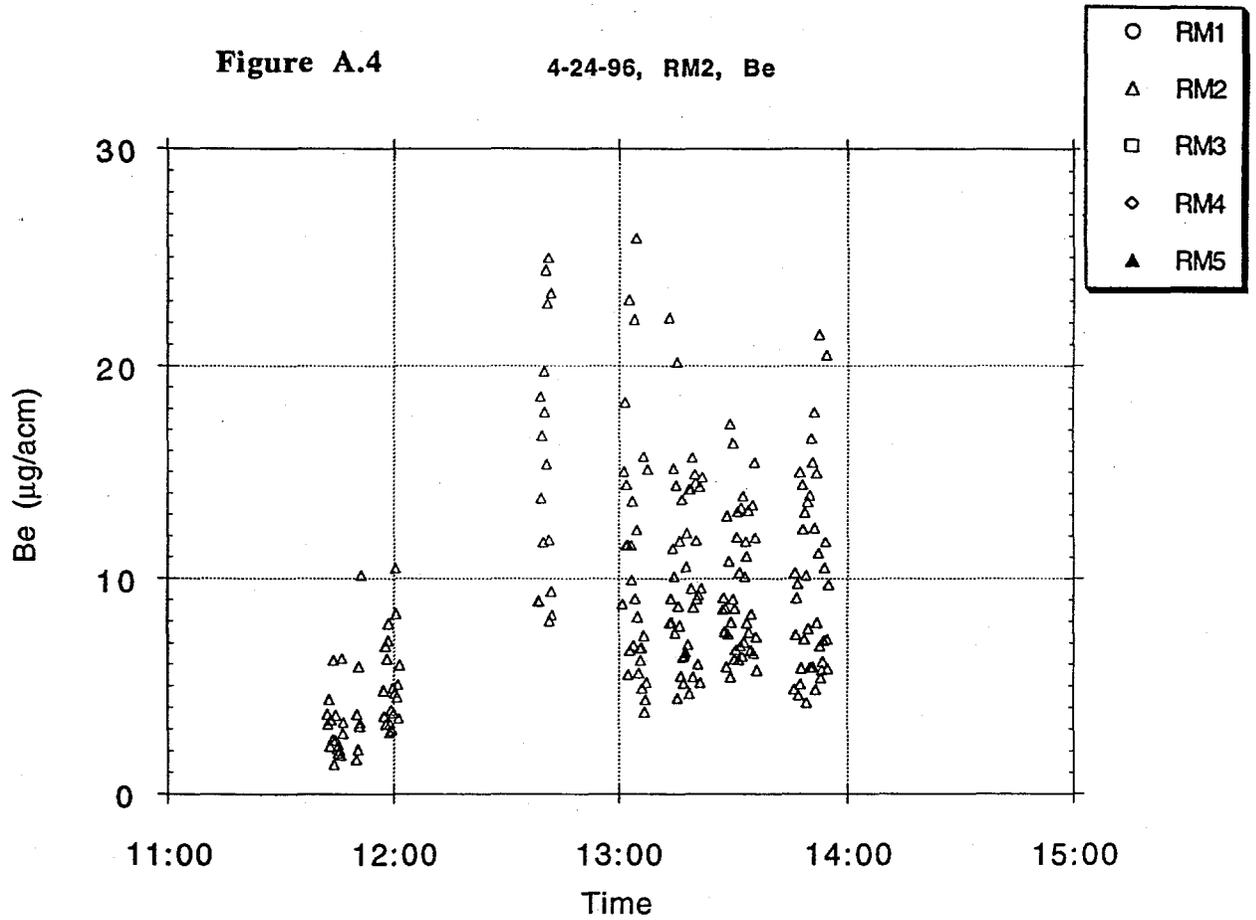
Appendix A: Metal-Concentration Measurements during Reference-Method Sampling Periods

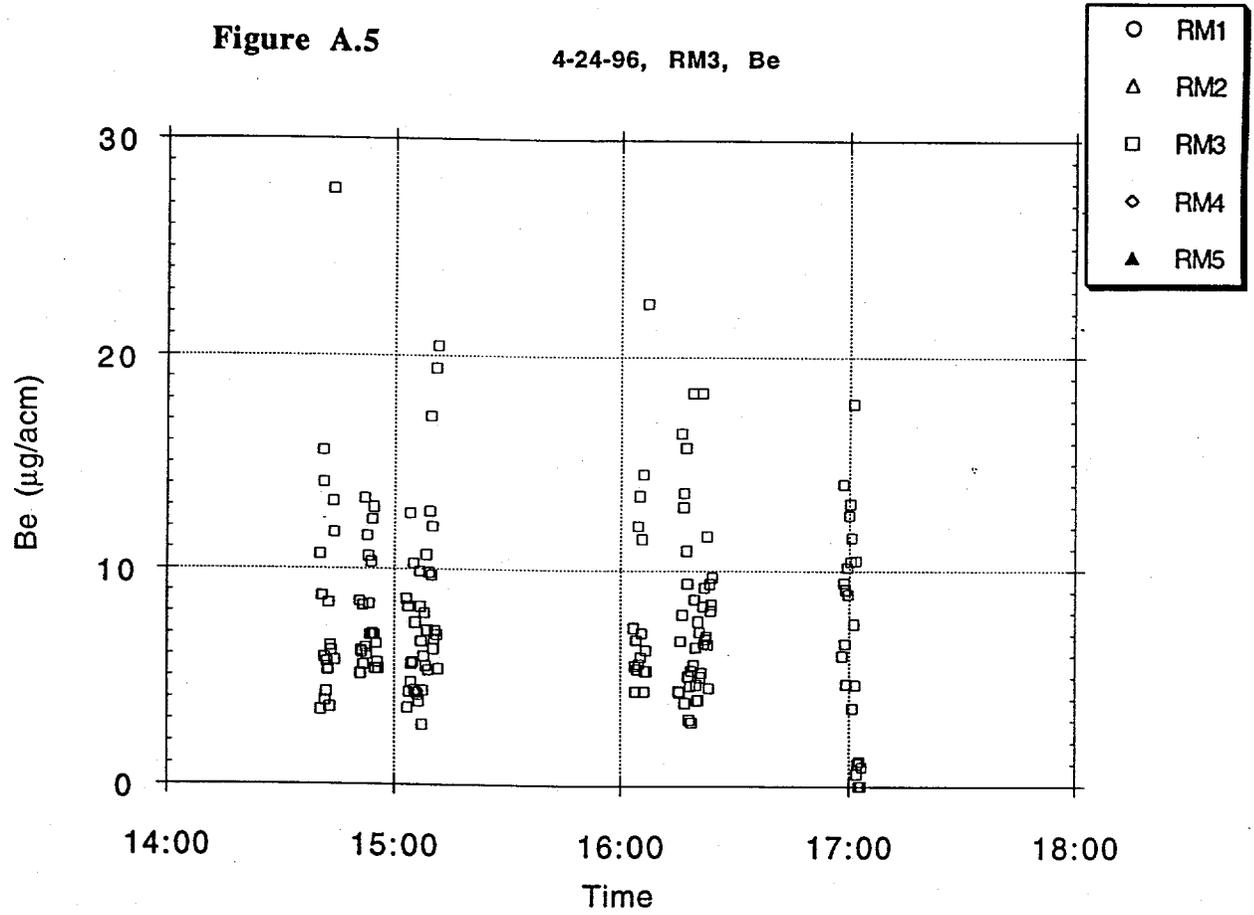
Figure A.2

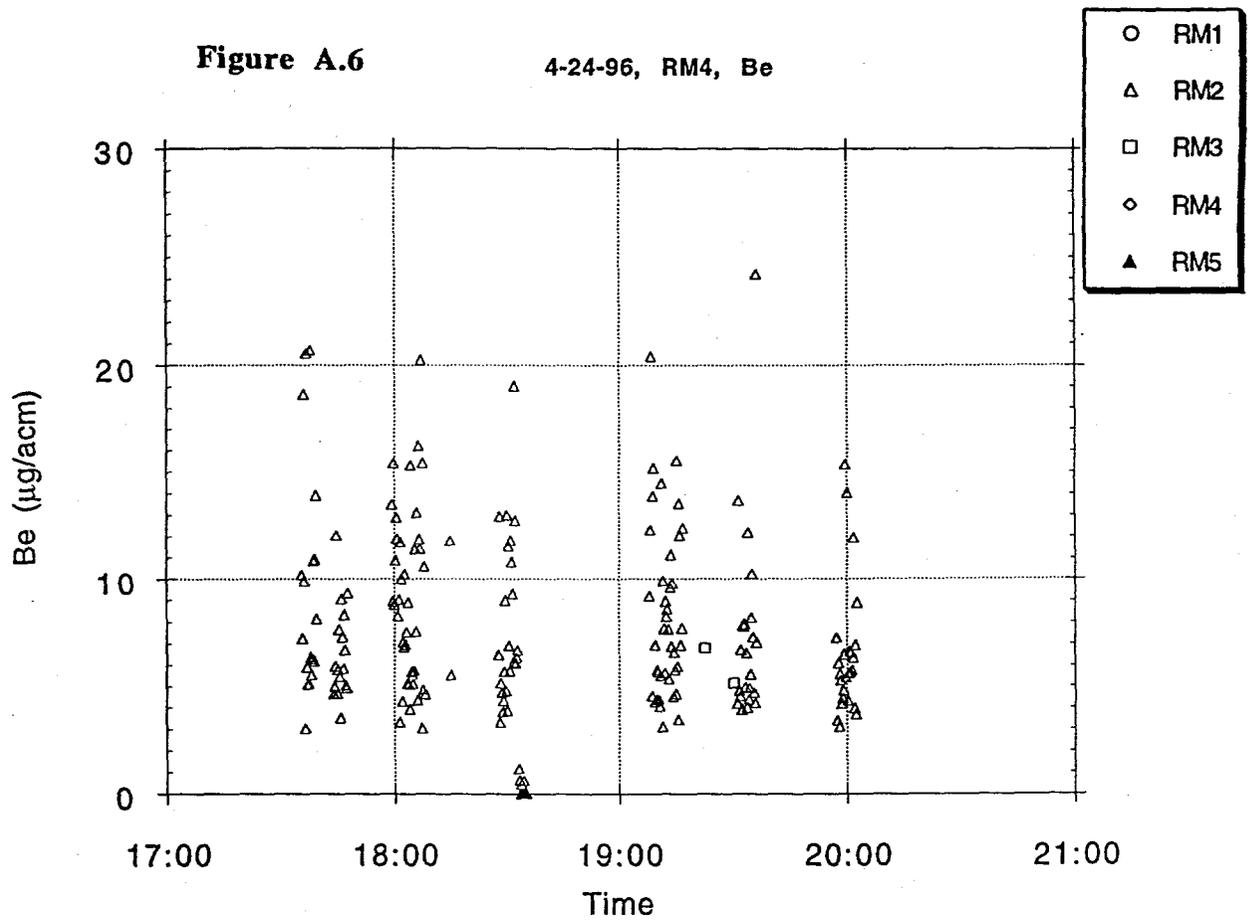
4-22-96, all RMs, Cd











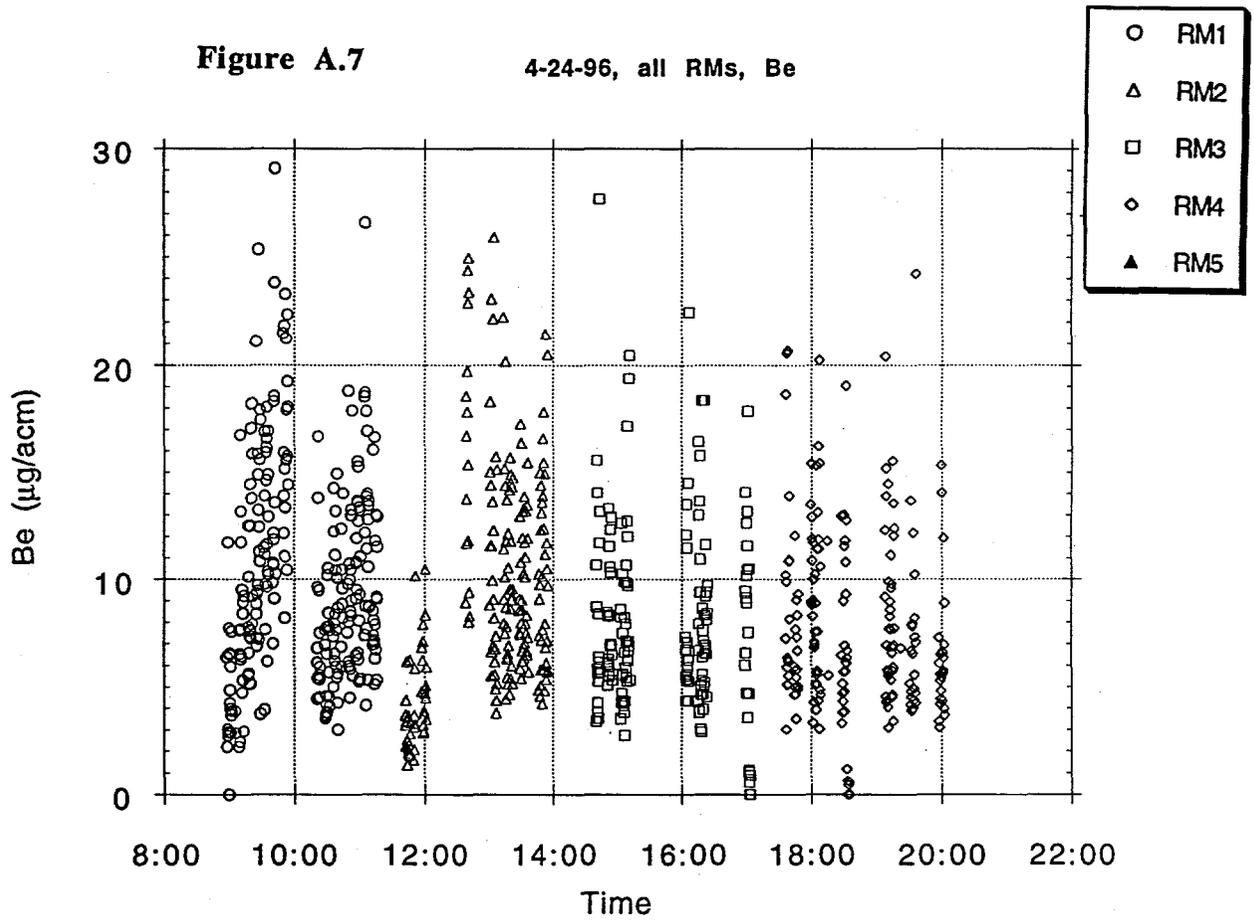
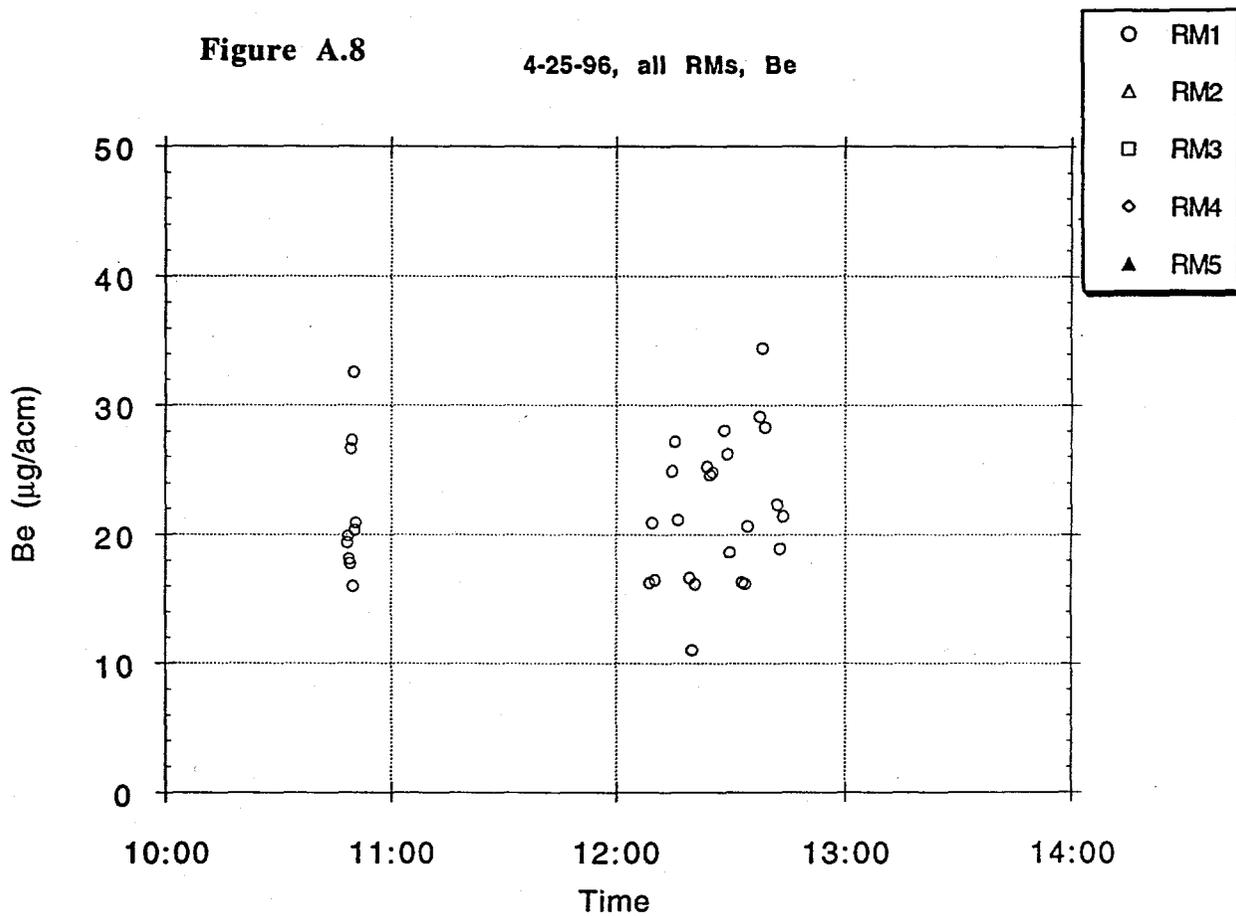
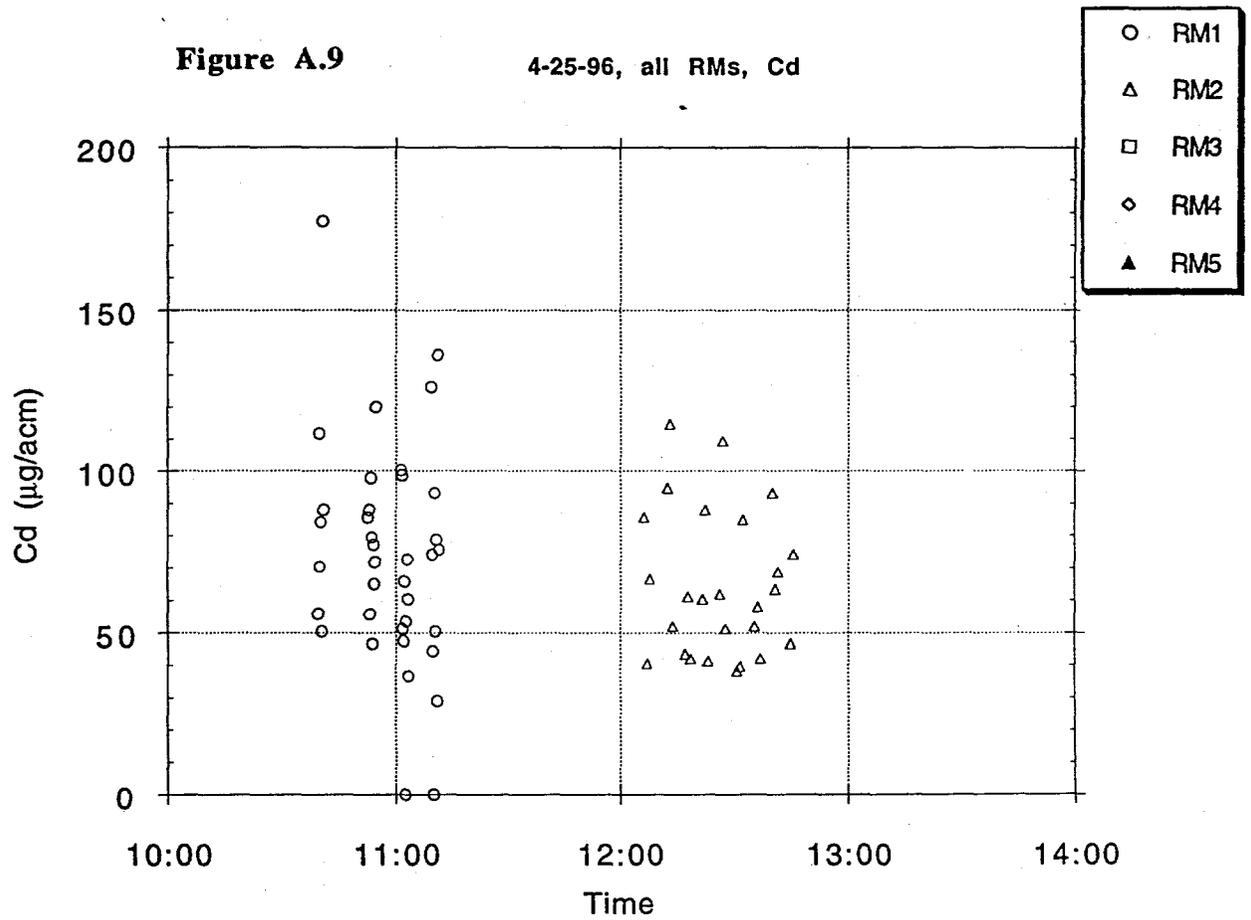


Figure A.8

4-25-96, all RMs, Be





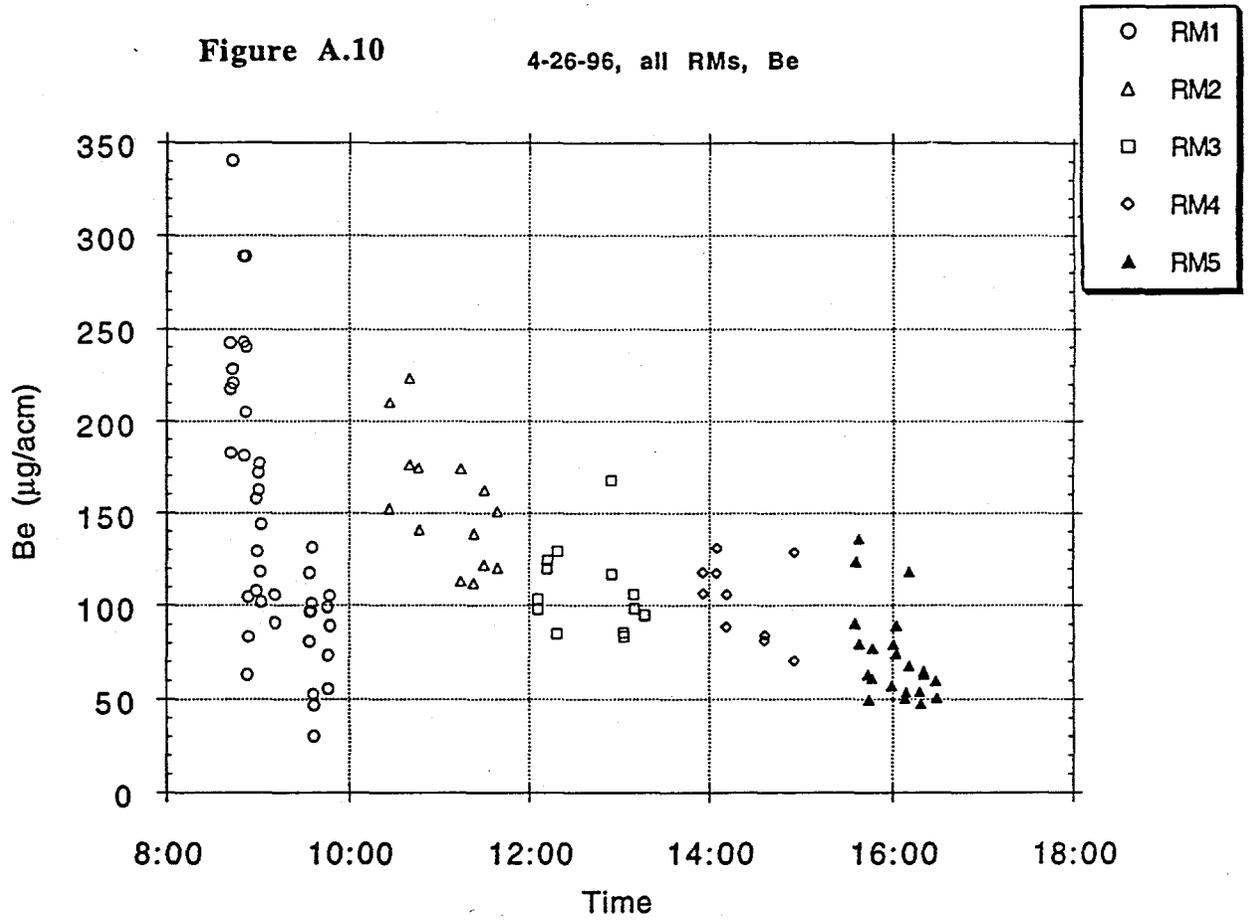
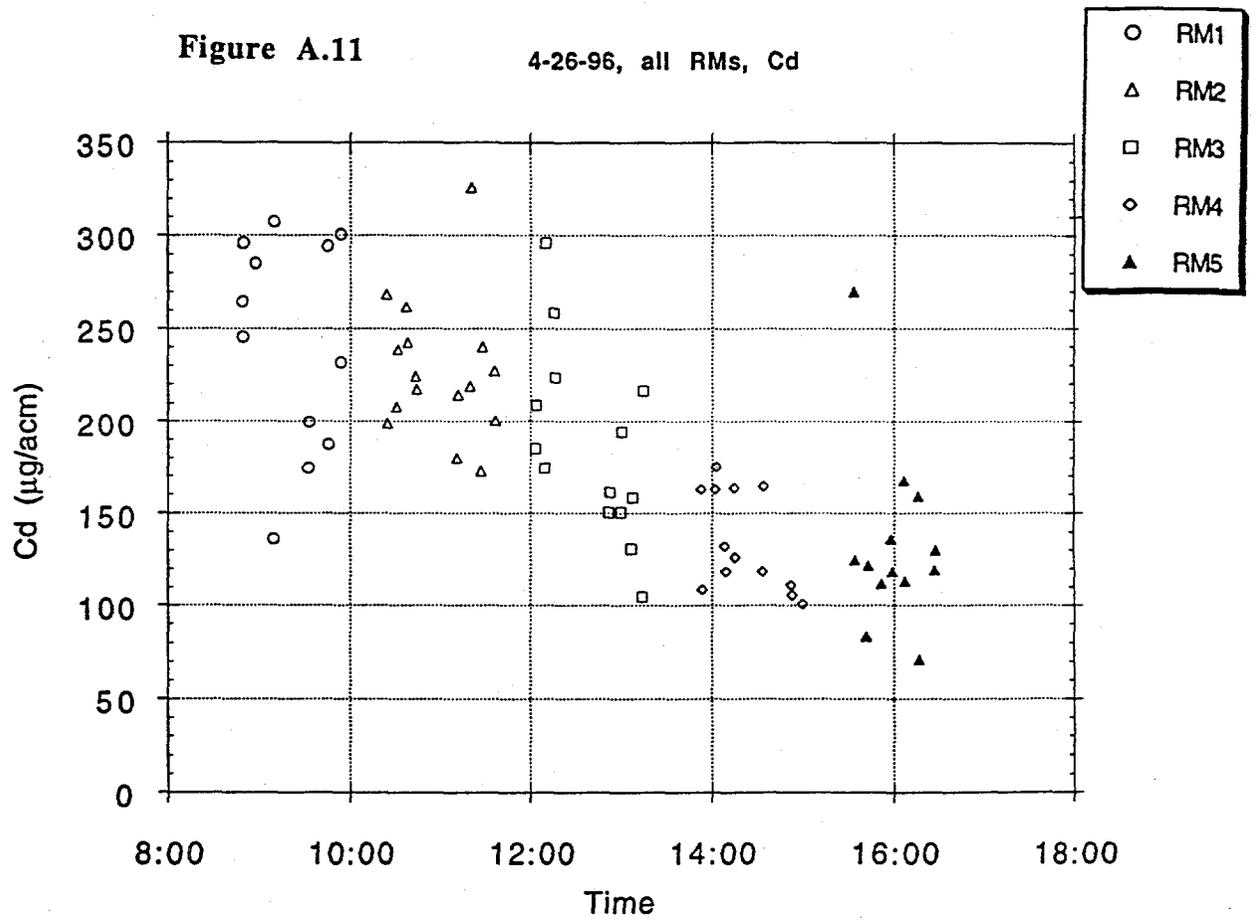
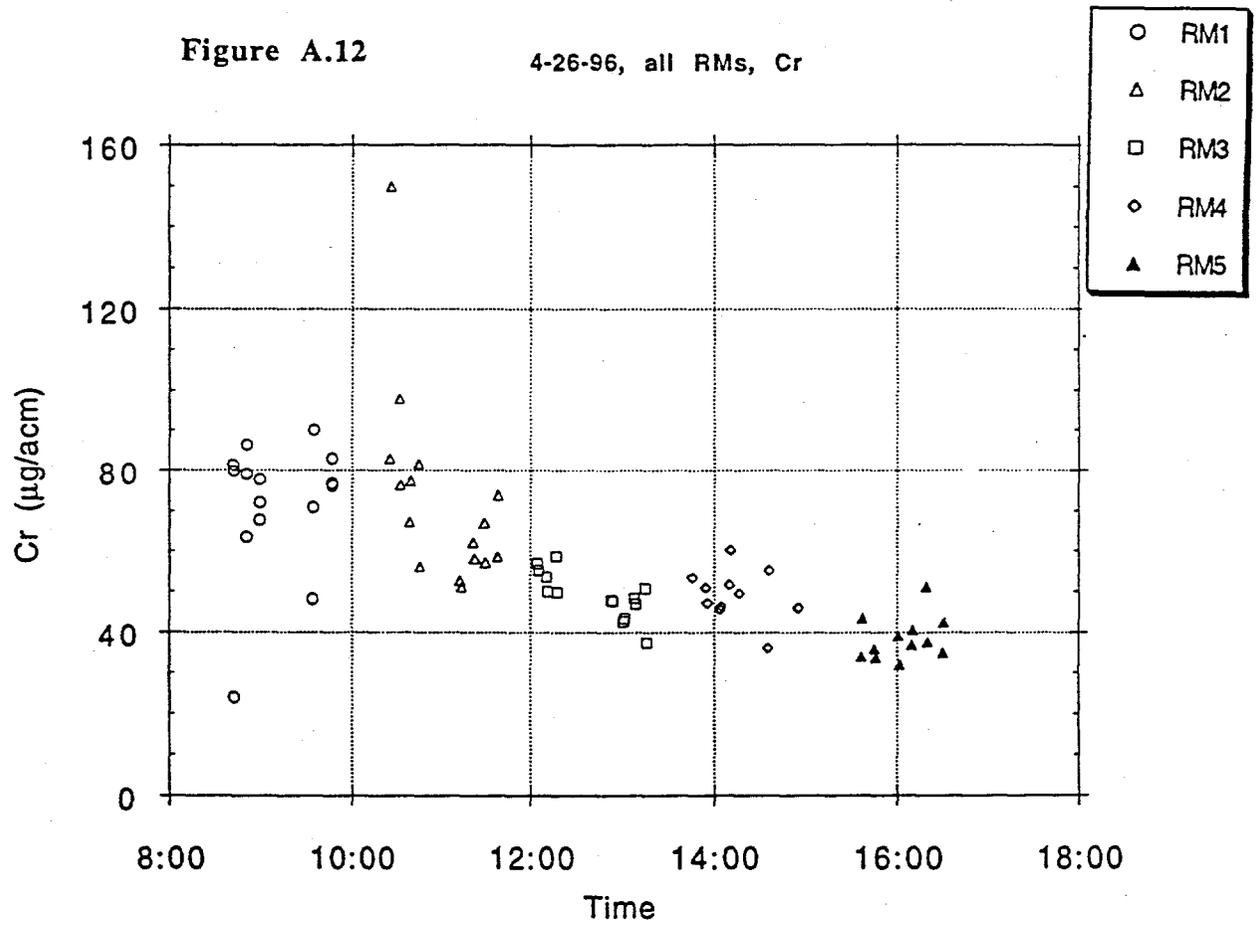
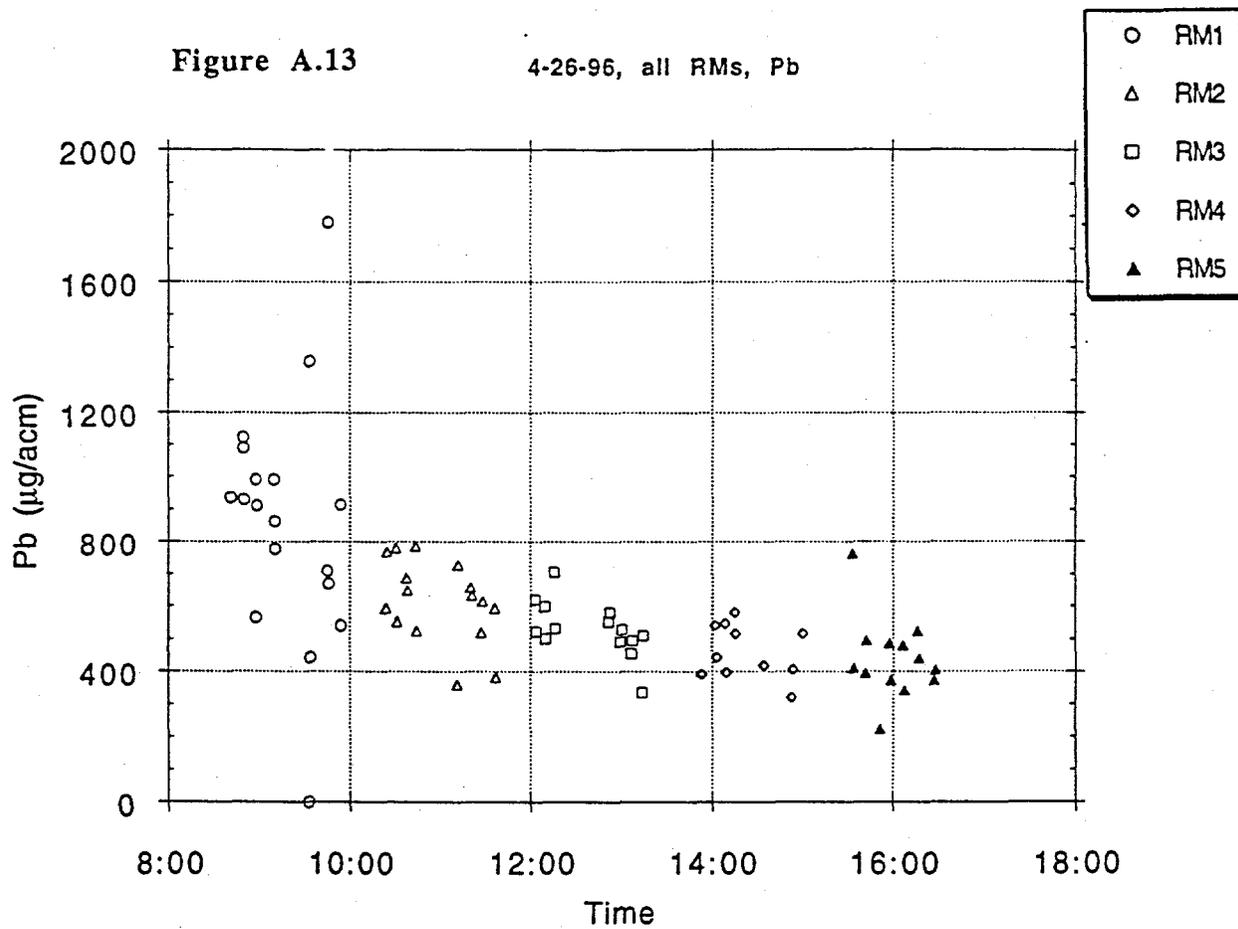


Figure A.11

4-26-96, all RMs, Cd







APPENDIX G
DEVELOPER TEAM
COMMENTS

APPENDIX G - DEVELOPER TEAM COMMENTS

Each CEM developer team was offered the opportunity to review the draft of this test report and, based on this review, to submit "developer team comments" for inclusion, without modification, in this final test report.

Comments from DIAL LIBS Team. Received 13. January 1997.

"DIAL team performed zero drift check every day before and after measurement during the CEM test. Zero concentration were found before fly ash and metal injection. No appreciable drift were observed during the tests. These observations have not been mentioned in the DIAL final report. The dichroic mirror was damaged during the last test day due to high humidity. This reduces the signal as well as the background in the spectra. The background signal was used to correct the LIBS signal. Thus, the measurements were only slightly degraded by the mirror damage.

LIBS data of metal concentrations versus time was provided to the program committee in the morning of second test day (April 24). The data format was acceptable to the committee and other developers were asked to submit the data with a similar format. The LIBS group noticed the slow increase in the concentration in the gas stream. This observation was immediately reported to the program committee.

The DIAL LIBS group detected the problem with the fly ash-metal injection system on the last test day (April 26) at 9:30am. The facility operator was informed of the problem. The facility control showed no sign of the effect at that time. It took some 20 minutes before the problem was recognized by the facility monitors which was then corrected immediately. The real-time, on-line CEM operation of LIBS has saved the full day operation of the test run for the facility and other CEM developers. This incident shows the importance and need for a CEM which can also be used a process control monitor.

Future Development:

Work on improving availability and detection sensitivity will be our main focus in future development. The existing calibration system will be modified to provide an on-line calibration of the LIBS system, as desired during the measurement. An auto calibration routine will be incorporated in the data processing software to correct the calibration factor for change in laser power and gas stream environments. The LIBS system will also be reconfigured to reduce the size of the system and will be purged with dry nitrogen to protect LIBS optics from laser damage due to moisture."

Comments from Navy/TJA Team Leader. Received 3 July 1997.

Developer Comments for CEM Report
U.S. Navy/Thermo Jarrell Ash
TraceAIR ICAP-Based Multimetals CEM

The April 1996 DOE/EPA sponsored multimetals CEM test at the EPA Research Center was the maiden field installation of the TraceAIR multimetals CEM. The TraceAIR was developed jointly by the Naval Air Warfare Center Weapons Division and Thermo Jarrell Ash Corporation under U.S. Army Demil Technology Office Sponsorship. When the April test schedule was first announced, laboratory assembly the TraceAIR system was near completion and preparations were underway for an initial field test, scheduled to take place in the Fall of 1996 at Tooele Army Depot, Utah. To accommodate the April test schedule, TraceAIR preparations, including mounting the entire CEM system in a trailer, had to be accelerated, resulting in the postponement of several critical tasks. Most important among these tasks was operation of the TraceAIR under simulated stack conditions. This was to be accomplished by obtaining a gas mixture containing molecular gases typically found in stack emissions, including, in appropriate concentrations, carbon dioxide, carbon monoxide, nitric oxide, and hydrocarbons. This gas mixture was to be used to determine the extent of spectral interferences that might arise from these species or reaction products thereof, and any other perturbations that might arise due to the presence of these gases in the inductively coupled plasma.

Inability to carry out these studies prior to the April tests put the TraceAIR CEM system at a considerable disadvantage since these tests represented the TraceAIR's first encounter with actual stack gases. The developers anticipated that a pre-test opportunity to sample stack gas from the EPA incinerator might provide valuable insight into the existence of spectral interferences and other perturbative phenomena and thus offer some advantage towards mitigating the effects of these factors on analytical results. However, when the TraceAIR arrived at the test site, it was discovered that the main power supply for the ICAP instrument had been damaged in transit. A replacement unit was obtained, but not in sufficient time to allow adequate pre-test examination of the effects of stack gas composition on plasma excitation of HAP metals and implementation of strategies to correct these effects. Consequently, the TraceAIR CEM began the test schedule without adequate preparation.

Spectral Interferences Due to Molecular Gases

On Monday, April 22, CEM testing commenced with the introduction of a medium level metal spike during which a number of reference method runs were carried out. Prior to the introduction of metals, the TraceAIR registered concentrations for several metals that were far in excess of their respective detection limits. For example, approximately 80 and 35 micrograms per dry standard cubic meter were detected for arsenic and selenium, respectively. This suggested the possible presence of spectral interferences. This was later confirmed by observing actual emission spectra. The interferences were attributed to emission from the CN radical, a

nascent molecular species formed in the plasma as a result of a reaction between carbon dioxide and nitrogen in stack gas. Post-test spectral subtraction was moderately successful in minimizing the extent of the interference for one or two of the affected HAP metals but was not feasible for many others because of the physical manifestation of the interference. A similar spectral interference was noted for mercury due to the coincidence of a nitric oxide emission band with the mercury emission line at 253.6 nm. Since the April tests, a proprietary method has been developed that actively and effectively corrects for this type of spectral interference, thereby eliminating completely, its contribution to measurement inaccuracy.

Suppression of Plasma Excitation

Inspection of comparative results (TraceAIR vs. reference method) indicated that several of the HAP metal (Pb, Cr, Hg) CEM measurements were systematically and consistently low relative to their reference method counterparts. These discrepancies were initially attributed to calibration errors. The TraceAIR developers have subsequently demonstrated that the presence of 5-7 percent carbon dioxide in sample air results in partial suppression of plasma excitation and subsequent emission intensity for several elements. Since calibration was carried out in pure ambient air, containing only nominal amounts of carbon dioxide, it is reasonable to assume that detection of metals in stack air containing appreciable amounts of carbon dioxide, was compromised to a certain extent by this phenomenon. The 30-40 percent suppression of excitation and emission for Pb, Cr, Hg recently confirmed by the TraceAIR developers by artificially introducing carbon dioxide along with airborne aerosols of these metals, explains to a large degree, the similar-sized discrepancies observed in their measurements *at all spiking levels*. We have since developed a calibration scheme that incorporates introduction of carbon dioxide along with calibration aerosols to ensure that calibration is accomplished under conditions nearly identical to those existing with introduction of actual stack air into the plasma. This approach completely mitigates the deleterious effects described above and will help ensure that higher accuracy can be achieved.

Plasma Torch Degradation

Prior to announcement of the April tests, a concerted effort had begun to optimize the geometry of the plasma torch used to accomplish injection of sample air into the argon plasma. This effort was in response to a series of problems associated with thermal degradation of the quartz plasma torches that resulted in unstable operation. As a result of systematic optimization, a unique modification of the standard plasma torch geometry has been implemented that now delivers satisfactory analytical performance and adequately lengthy torch life. Unfortunately, torches of the new design were not available in time for the April tests requiring the use of standard plasma torches designed for pure argon plasma operation. These torches degraded rapidly during the April tests and analytical performance was degraded accordingly.

Sample Transport

The TraceAIR multimetals CEM is an extractive method that relies on pneumatic transport of sample air from the stack to the CEM. Optimization of the transport process is essential to achieving accurate results. During the April tests, efficient sample transport was not achieved for the following reasons.

Section 2.1 of the draft CEM report states that the air velocity in the sampling duct is 5.7 - 9.6 ft/sec. Similar values were provided to the developers at the organizational meeting at RTP prior to the April tests. At the beginning of the tests, the actual duct velocity measured independently by Navy/TJA and Accurex was 26-27 ft/sec. As indicated in my earlier post-test comments, using the 5.7 - 9.6 ft/sec velocity previously provided, I calculated that a isokinetic sampling nozzle of 1/2" diameter would be required and subsequently, I purchased this item. However, upon discovering that the actual velocity was much higher as a result of EPA's need to add dilution air to cool the flue gases (ref: Paul Lemieux), I had no option other than to use an alternate nozzle size, 1/4". (The 1/2" nozzle would have required a sampling rate in excess of 30 SLM, much beyond the capability of the existing extraction hardware) Unfortunately, 1/4" was the only other size that I had at the time. The 1/4" nozzle required a volumetric sampling rate of around 8.5 SLM to achieve isokinetic extraction under the existing duct conditions. The 8.5 liter per minute flow rate was apparently not adequate to promote efficient sample transport through the 75 feet of sample line to the TraceAIR CEM. Following the April tests, it was confirmed experimentally that there were modest particulate losses in the sample line and these losses have been attribute to this factor. A complete set of sampling nozzles has since been purchased to accommodate a wide range of stack conditions and permit selection of a nozzle size that will allow use of the highest possible sampling flow rate.

Summary

The phenomena described above acted in concert to compromise the analytical performance of the TraceAIR multimetals CEM during its maiden field installation. Rectification of problems associated with these phenomena is solely the responsibility of the developers. Since the April tests, most of the problems described above have been eliminated and the TraceAIR CEM has performed well in conjunction with a variety of large scale combustors including a hazardous waste incinerator, a coal-fired power plant, and a military explosive ordnance furnace.

A recommendation for future test programs similar to that held in April, 1996, is that more advanced notification should be made, thereby affording the developers a fair opportunity to make necessary preparations.

APPENDIX H

PERFORMANCE SPECIFICATION 10

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SPECIFICATIONS AND TEST PROCEDURES FOR MULTI-METALS CONTINUOUS MONITORING SYSTEMS IN STATIONARY SOURCES

60, Appendix B, Performance Specification 3), (b) flow monitoring equipment to allow measurement of the dry volume of stack effluent sampled, and (c) an automatic sampling system.

A multi-metals CEMS must be capable of measuring the total concentrations (regardless of speciation) of two or more of the following metals in both their vapor and solid forms: Antimony (Sb), Arsenic (As), Barium (Ba), Beryllium (Be), Cadmium (Cd), Chromium (Cr), Lead (Pb), Mercury (Hg), Silver (Ag), Thallium (Tl), Manganese (Mn), Cobalt (Co), Nickel (Ni), and Selenium (Se). Additional metals may be added to this list at a later date by addition of appendices to this performance specification. If a CEMS does not measure a particular metal or fails to meet the performance specifications for a particular metal, then the CEMS may not be used to determine emission compliance with the applicable regulation for that metal.

This specification is not designed to evaluate the installed CEMS' performance over an extended period of time nor does it identify specific calibration techniques and auxiliary procedures to assess the CEMS' performance. The source owner or operator, however, is responsible to properly calibrate, maintain, and operate the CEMS. To evaluate the CEMS' performance, the Administrator may require, under Section 114 of the Act, the operator to conduct CEMS performance evaluations at other times besides the initial

test. See Sec. 60.13 (c) and "Quality Assurance Requirements For Multi-Metals Continuous Emission Monitoring Systems Used For Compliance Determination."

1.2 Principle. Installation and measurement location specifications, performance specifications, test procedures, and data reduction procedures are included in this specification. Reference method tests and calibration drift tests are conducted to determine conformance of the CEMS with the specification.

2. Definitions

2.1 Continuous Emission Monitoring System (CEMS). The total equipment required for the determination of a metal concentration. The system consists of the following major subsystems:

2.1.1 Sample Interface. That portion of the CEMS used for one or more of the following: sample acquisition, sample transport, and sample conditioning, or protection of the monitor from the effects of the stack effluent.

2.1.2 Pollutant Analyzer. That portion of the CEMS that senses the metals concentrations and generates a proportional output.

2.1.3 Diluent Analyzer (if applicable). That portion of the CEMS that senses the diluent gas (O₂) and generates an output proportional to the gas concentration.

Performance Specification 10
Specifications and test procedures for multi-metals continuous monitoring systems in stationary sources.

1. Applicability and Principle

1.1 Applicability. This specification is to be used for evaluating the acceptability of multi-metals continuous emission monitoring systems (CEMS) at the time of or soon after installation and whenever specified in the regulations. The CEMS may include, for certain stationary sources, (a) a diluent (O₂) monitor (which must meet its own performance specifications: 40 CFR part

2.1.4 Data Recorder. That portion of the CEMS that provides a permanent record of the analyzer output. The data recorder may provide automatic data reduction and CEMS control capabilities.

2.2 Point CEMS. A CEMS that measures the metals concentrations either at a single point or along a path equal to or less than 10 percent of the equivalent diameter of the stack or duct cross section.

2.3 Path CEMS. A CEMS that measures the metals concentrations along a path greater than 10 percent of the equivalent diameter of the stack or duct cross section.

2.4 Span Value. The upper limit of a metals concentration measurement range defined as twenty times the applicable emission limit for each metal. The span value shall be documented by the CEMS manufacturer with laboratory data.

2.5 Relative Accuracy (RA). The absolute mean difference between the metals concentrations determined by the CEMS and the value determined by the reference method (RM) plus the 2.5 percent error confidence coefficient of a series of tests divided by the mean of the RM tests or the applicable emission limit.

2.6 Calibration Drift (CD). The difference in the CEMS output readings from the established reference value after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

2.7 Zero Drift (ZD). The difference in the CEMS output readings for zero input after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

2.8 Representative Results. Defined by the RA test procedure defined in this specification.

2.9 Response Time. The time interval between the start of a step change in the system input and the time when the pollutant analyzer output reaches 95 percent of the final value.

2.10 Centroidal Area. A concentric area that is geometrically similar to the stack or duct cross section and is no greater than 1 percent of the stack or duct cross sectional area.

2.11 Batch Sampling. Batch sampling refers to the technique of sampling the stack effluent continuously and concentrating the pollutant in some capture medium. Analysis is performed periodically after sufficient time has elapsed to concentrate the pollutant to levels detectable by the analyzer.

2.12 Calibration Standard. Calibration standards consist of a known amount of metal(s) that are presented to the pollutant analyzer portion of the CEMS in order to calibrate the drift or response of the analyzer. The calibration standard may be, for example, a solution containing a known metal concentration, or a filter with a known mass loading or composition.

3. Installation and Measurement Location Specifications

3.1 The CEMS Installation and measurement location. Install the CEMS at an accessible location downstream of all pollution control equipment where the metals concentrations measurements are

directly representative or can be corrected so as to be representative of the total emissions from the affected facility. Then select representative measurement points or paths for monitoring in locations that the CEMS will pass the RA test (see Section 7). If the cause of failure to meet the RA test is determined to be the measurement location and a satisfactory correction technique cannot be established, the Administrator may require the CEMS to be relocated.

Measurement locations and points or paths that are most likely to provide data that will meet the RA requirements are listed below.

3.1.1 Measurement Location. The measurement location should be (1) at least eight equivalent diameters downstream of the nearest control device, point of pollutant generation, bend, or other point at which a change of pollutant concentration or flow disturbance may occur, and (2) at least two equivalent diameters upstream from the effluent exhaust. The equivalent duct diameter is calculated as per 40 CFR part 60, Appendix A, Method 1, Section 2.1.

3.1.2 Point CEMS. The measurement point should be (1) no less than 1.0 meter from the stack or duct wall or (2) within or centrally located over the centroidal area of the stack or duct cross section. Selection of traverse points to determine the representativeness of the measurement location should be made according to 40 CFR part 60, Appendix A, Method 1, Sections 2.2 and 2.3.

3.1.3 Path CEMS. The effective measurement path should be (1) totally within the inner area bounded by a line 1.0 meter from the stack or duct wall, or (2) have at least 70 percent of the path within the inner 50 percent of the stack or duct cross sectional area, or (3) be centrally located over any part of the centroidal area.

3.2 Reference Method (RM) Measurement Location and Traverse Points. The RM measurement location should be (1) at least eight equivalent diameters downstream of the nearest control device, point of pollutant generation, bend, or other point at which a change of pollutant concentration or flow disturbance may occur, and (2) at least two equivalent diameters upstream from the effluent exhaust. The RM and CEMS locations need not be the same, however the difference may contribute to failure of the CEMS to pass the RA test, thus they should be as close as possible without causing interference with one another. The equivalent duct diameter is calculated as per 40 CFR part 60, Appendix A, Method 1, Section 2.1. Selection of traverse measurement point locations should be made according to 40 CFR part 60, Appendix A, Method 1, Sections 2.2 and 2.3. If the RM traverse line interferes with or is interfered by the CEMS measurements, the line may be displaced up to 30 cm (or 5 percent of the equivalent diameter of the cross section, whichever is less) from the centroidal area.

4. Performance and Equipment Specifications

4.1 Data Recorder Scale. The CEMS data recorder response range must include zero and a high level value. The high level value must be equal to the span value. If a lower

high level value is used, the CEMS must have the capability of providing multiple outputs with different high level values (one of which is equal to the span value) or be capable of automatically changing the high level value as required (up to the span value) such that the measured value does not exceed 95 percent of the high level value.

4.2 Relative Accuracy (RA). The RA of the CEMS must be no greater than 20 percent of the mean value of the RM test data in terms of units of the emission standard for each metal, or 10 percent of the applicable standard, whichever is greater.

4.3 Calibration Drift. The CEMS design must allow the determination of calibration drift at concentration levels commensurate with the applicable emission standard for each metal monitored. The CEMS calibration may not drift or deviate from the reference value (RV) of the calibration standard used for each metal by more than 5 percent of the emission standard for each metal. The calibration shall be performed at a point equal to 80 to 120 percent of the applicable emission standard for each metal.

4.4 Zero Drift. The CEMS design must allow the determination of calibration drift at the zero level (zero drift) for each metal. If this is not possible or practicable, the design must allow the zero drift determination to be made at a low level value (zero to 20 percent of the emission limit value). The CEMS zero point for each metal shall not drift by more than 5 percent of the emission standard for that metal.

4.5 Sampling and Response Time. The CEMS shall sample the stack effluent continuously. Averaging time, the number of measurements in an average, and the averaging procedure for reporting and determining compliance shall conform with that specified in the applicable emission regulation.

4.5.1 Response Time for Instantaneous, Continuous CEMS. The response time for the CEMS must not exceed 2 minutes to achieve 95 percent of the final stable value.

4.5.2 Waiver from Response Time Requirement. A source owner or operator may receive a waiver from the response time requirement for instantaneous, continuous CEMS in section 4.5.1 from the Agency if no CEM is available which can meet this specification at the time of purchase of the CEMS.

4.5.3 Response Time for Batch CEMS. The response time requirement of Sections 4.5.1 and 4.5.2 do not apply to batch CEMS. Instead it is required that the sampling time be no longer than one third of the averaging period for the applicable standard. In addition, the delay between the end of the sampling period and reporting of the sample analysis shall be no greater than one hour. Sampling is also required to be continuous except in that the pause in sampling when the sample collection media are changed should be no greater than five percent of the averaging period or five minutes, whichever is less.

5. Performance Specification Test Procedure

5.1 Pretest Preparation. Install the CEMS and prepare the RM test site according to the specifications in Section 3, and prepare the

CEMS for operation according to the manufacturer's written instructions.

5.2 Calibration and Zero Drift Test Period. While the affected facility is operating at more than 50 percent of normal load, or as specified in an applicable subpart, determine the magnitude of the calibration drift (CD) and zero drift (ZD) once each day (at 24-hour intervals) for 7 consecutive days according to the procedure given in Section 6. To meet the requirements of Sections 4.3 and 4.4 none of the CD's or ZD's may exceed the specification. All CD determinations must be made following a 24-hour period during which no unscheduled maintenance, repair, or manual adjustment of the CEMS took place.

5.3 RA Test Period. Conduct a RA test following the CD test period. Conduct the RA test according to the procedure given in Section 7 while the affected facility is operating at more than 50 percent of normal load, or as specified in the applicable subpart.

6.0 The CEMS Calibration and Zero Drift Test Procedure

This performance specification is designed to allow calibration of the CEMS by use of standard solutions, filters, etc. that challenge the pollutant analyzer part of the CEMS (and as much of the whole system as possible), but which do not challenge the entire CEMS, including the sampling interface. Satisfactory response of the entire system is covered by the RA requirements.

The CD measurement is to verify the ability of the CEMS to conform to the established CEMS calibration used for determining the emission concentration. Therefore, if periodic automatic or manual adjustments are made to the CEMS zero and calibration settings, conduct the CD test immediately before the adjustments, or conduct it in such a way that the CD and ZD can be determined.

Conduct the CD and ZD tests at the points specified in Sections 4.3 and 4.4. Record the CEMS response and calculate the CD according to:

$$CD = \frac{(R_{CEM} - R_V)}{R_V} \times 100, \quad (1)$$

Where CD denotes the calibration drift of the CEMS in percent, R_{CEM} is the CEMS response, and R_V is the reference value of the high level calibration standard. Calculate the ZD according to:

$$ZD = \frac{(R_{CEM} - R_{EM})}{R_{EM}} \times 100, \quad (2)$$

Where ZD denotes the zero drift of the CEMS in percent, R_{CEM} is the CEMS response, R_V is the reference value of the low level calibration standard, and R_{EM} is the emission limit value.

7. Relative Accuracy Test Procedure

7.1 Sampling Strategy for RA Tests. The RA tests are to verify the initial performance

of the entire CEMS system, including the sampling interface, by comparison to RM measurements. Conduct the RM measurements in such a way that they will yield results representative of the emissions from the source and can be correlated to the CEMS data. Although it is preferable to conduct the diluent (if applicable), moisture (if needed), and pollutant measurements simultaneously, the diluent and moisture measurements that are taken within a 30 to 60-minute period, which includes the pollutant measurements, may be used to calculate dry pollutant concentration.

A measure of relative accuracy at a single level is required for each metal measured for compliance purposes by the CEMS. Thus the concentration of each metal must be detectable by both the CEMS and the RM. In addition, the RA must be determined at three levels (0 to 20, 40 to 60, and 80 to 120 percent of the emission limit) for one of the metals which will be monitored, or for iron. If iron is chosen, the three levels should be chosen to correspond to those for one of the metals that will be monitored using known sensitivities (documented by the manufacturer) of the CEMS to both metals.

In order to correlate the CEMS and RM data properly, note the beginning and end of each RM test period of each run (including the exact time of day) in the CEMS data log. Use the following strategy for the RM measurements:

7.2 Correlation of RM and CEMS Data. Correlate the CEMS and RM test data as to the time and duration by first determining from the CEMS final output (the one used for reporting) the integrated average pollutant concentration for each RM test period. Consider system response time, if important, and confirm that the pair of results are on a consistent moisture, temperature, and diluent concentration basis. Then compare each integrated CEMS value against the corresponding average RM value.

7.3 Number of tests. Obtain a minimum of three pairs of CEMS and RM measurements for each metal required and at each level required (see Section 7.1). If more than nine pairs of measurements are obtained, then up to three pairs of measurements may be rejected so long as the total number of measurement pairs used to determine the RA is greater than or equal to nine. However, all data, including the rejected data, must be reported.

7.4 Reference Methods. Unless otherwise specified in an applicable subpart of the regulations, Method 3B, or its approved alternative, is the reference method for diluent (O_2) concentration. Unless otherwise specified in an applicable subpart of the regulations, the manual method for multi-metals in 40 CFR part 266, Appendix IX, Section 3.1 (until superseded by SW 846), or its approved alternative, is the reference method for multi-metals.

As of March 22, 1995 there is no approved alternative RM to Method 29 (for example, a second metals CEMS, calibrated absolutely according to the alternate procedure to be specified in an appendix to this performance

specification to be added when an absolute system calibration procedure becomes available and is approved).

7.5 Calculations. Summarize the results on a data sheet. An example is shown in Figure 2.2 of 40 CFR part 60, Appendix B, Performance Specification 2. Calculate the mean of the RM values. Calculate the arithmetic differences between the RM and CEMS output sets, and then calculate the mean of the differences. Calculate the standard deviation of each data set and CEMS RA using the equations in Section 8.

7.6 Undetectable Emission Levels. In the event of metals emissions concentrations from the source being so low as to be undetectable by the CEMS operating in its normal mode (i.e., measurement times and frequencies within the bounds of the performance specifications), then spiking of the appropriate metals in the feed or other operation of the facility in such a way as to raise the metal concentration to a level detectable by both the CEMS and the RM is required in order to perform the RA test.

8. Equations

8.1 Arithmetic Mean. Calculate the arithmetic mean of a data set as follows:

$$\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i, \quad (3)$$

Where n is equal to the number of data points.

8.1.1 Calculate the arithmetic mean of the difference, d , of a data set, using Equation 3 and substituting d for x . Then

$$d_i = x_i - y_i, \quad (4)$$

Where x and y are paired data points from the CEMS and RM, respectively.

8.2 Standard Deviation. Calculate the standard deviation (SD) of a data set as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^n x_i^2 - \frac{1}{n} \left(\sum_{i=1}^n x_i \right)^2}{n-1}}, \quad (5)$$

8.3 Relative Accuracy (RA). Calculate the RA as follows:

$$RA = \frac{\bar{d} + \frac{t_{0.975}}{\sqrt{n}} (SD)}{\bar{R}_{RM}}, \quad (6)$$

Where d is equal to the arithmetic mean of the difference, d , of the paired CEMS and RM data set, calculated according to Equations 3 and 4, SD is the standard deviation calculated according to Equation 5, \bar{R}_{RM} is equal to either the average of the RM data set, calculated according to Equation 3, or the value of the emission standard, as applicable (see Section 4.2), and $t_{0.975}$ is the t -value at 2.5 percent error confidence, see Table 1.

TABLE 1
[t-Values]

n ^a	t _{0.975}	n ^a	t _{0.975}	n ^a	t _{0.975}
2	12.706	7	2.447	12	2.201
3	4.303	8	2.365	13	2.179
4	3.182	9	2.306	14	2.160
5	2.776	10	2.262	15	2.145
6	2.571	11	2.228	16	2.131

^aThe values in this table are already corrected for n-1 degrees of freedom. Use n equal to the number of individual values.

9. Reporting

At a minimum (check with the appropriate regional office, or State, or local agency for additional requirements, if any) summarize in tabular form the results of the CD tests and the RA tests or alternate RA procedure as appropriate. Include all data sheets, calculations, and records of CEMS response necessary to substantiate that the performance of the CEMS met the performance specifications.

The CEMS measurements shall be reported to the agency in units of $\mu\text{g}/\text{m}^3$ on a dry basis, corrected to 20°C and 7 percent O₂.

10. Alternative Procedures

A procedure for a total system calibration, when developed, will be acceptable as a procedure for determining RA. Such a procedure will involve challenging the entire CEMS, including the sampling interface, with a known metals concentration. This procedure will be added as an appendix to this performance specification when it has been developed and approved. The RA requirement of Section 4.2 will remain unchanged.

11. Bibliography

1. 40 CFR part 60, Appendix B, "Performance Specification 2 Specifications and Test Procedures for SO₂ and NO_x Continuous Emission Monitoring Systems in Stationary Sources."

2. 40 CFR part 60, Appendix B, "Performance Specification 1 Specification and Test Procedures for Opacity Continuous Emission Monitoring Systems in Stationary Sources."

3. 40 CFR part 60, Appendix A, "Method 1 Sample and Velocity Traverses for Stationary Sources."

4. 40 CFR part 266, Appendix IX, Section 2, "Performance Specifications for Continuous Emission Monitoring Systems."

5. Draft Method 29, "Determination of Metals Emissions from Stationary Sources," Docket A 90 45, Item II B 12, and EMTIC CTM 012.WPF.

6. "Continuous Emission Monitoring Technology Survey for Incinerators, Boilers, and Industrial Furnaces: Final Report for Metals CEM's," prepared for the Office of Solid Waste, U.S. EPA, Contract No. 68 D2 0164 (4/25/94).