

ESTCP Cost and Performance Report

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Aerosol Beam Focused-Laser Induced Plasma Spectrometer (ABF-LIPS) Continuous Emissions Multi-Metals Analyzer

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ACRONYMS AND ABBREVIATIONS

ABF-LIPS	Aerosol Beam-Focused Laser-Induced Plasma Spectrometer
ACFM	actual cubic feet per minute
Ag	silver
Al	aluminum
APE	Ammunition Peculiar Equipment
As	arsenic
Ba	barium
Be	beryllium
BTU	British thermal unit
C	carbon
CD	calibration drift
Cd	cadmium
CEMS	continuous emission monitoring system
CFR	Code of Federal Regulations
CO	carbon monoxide
Co	cobalt
Cu	copper
Cr	chromium
DF	deactivation furnace
DI	deionized
DoD	U.S. Department of Defense
Dp	particle diameter
DSCF	dry standard cubic feet
DSCFM	dry standard cubic feet per minute
DSCM	dry standard cubic meter
USEPA	U.S. Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
Fe	iron
HAP	hazardous air pollutant
Hg	mercury
hp	horsepower
ICCD	intensified charge-coupled device
ICP	inductively coupled plasma
ID	inside diameter
L	liter
LIBS	laser-induced breakdown spectroscopy
µg	microgram
µm	micrometer
Mn	manganese

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mL	milliliter
MS	mass spectrometry
NADEP	Naval Aviation Depot
NAVFAC	Naval Facilities Engineering Command
Ni	nickel
nm	nanometer
O ₂	oxygen
O&M	operation and maintenance
ORNL	Oak Ridge National Laboratory
Pb	lead
PES	Professional Environmental Services, Inc.
PLC	programmable logic controller
ppm	parts per million
PS	performance specification
RA	relative accuracy
RM	reference method
rpm	revolutions per minute
RV	reference value
S	sulfur
Sb	antimony
scfm	standard cubic feet per minute
SD	standard deviation
Se	selenium
SERDP	Strategic Environmental Research and Development Program
TEAD	Tooele Army Depot
Tl	thallium
WFRMS	waste feed rate monitoring system
XCEMS	x-ray continuous emission monitoring system
XRF	x-ray fluorescence
ZD	zero drift
Zn	zinc

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1.0 EXECUTIVE SUMMARY

1.1 BACKGROUND

This report describes field testing of a novel continuous emissions metals analyzer, the Aerosol Beam-Focused Laser-Induced Plasma Spectrometer (ABF-LIPS), developed by Oak Ridge National Laboratory (ORNL) in the laboratory of Dr. Meng-Dawn Cheng. Continuous emission monitoring systems (CEMS) provide an effective means for monitoring the level of hazardous air pollutants (HAP) in real time, potentially allowing for better control of processes and improved pollution control without relying on conservative permit limits, which are based on time-averaged integrated traditional sampling techniques with off-site laboratory determination of HAPs.

The principle of operation of ABF-LIPS is a pulsed laser beam tightly focused onto an aerosol sample to ignite a plasma, which breaks down all compounds to their elemental composition. The elements in the plasma volume are vaporized, resulting in an unstable, excited state. When the atoms return from the plasma-excited state to ground, they release light at element-specific wavelengths that can be observed using time-resolved spectroscopy. The wavelengths of the emission spectra correspond to a particular element, and the amplitudes of the peaks correspond to the mass of that element. The aerosol beam focusing capability improves the detection and sensitivity of traditional laser induced plasma spectrometry by aerodynamically focusing aerosol particles to a point, increasing the local aerosol concentration and significantly improving the signal-to-noise ratio. ABF-LIPS, because of its portability, can be mounted at an emission source and requires no long sampling line, which virtually eliminates sample loss.

1.2 DEMONSTRATION OBJECTIVES AND PROCEDURES

The ABF-LIPS instrument was tested on three sources at the Naval Aviation Depot (NADEP), San Diego, including a metals plating shop and a molten metal casting furnace, and at a munitions deactivation incinerator at Tooele Army Depot (TEAD). The facilities were selected to test the instrument under varying conditions in real-world settings. The demonstration objectives were to obtain data under real-world conditions to complement laboratory data and previous field testing. The performance criteria included: (1) analytical performance: relative accuracy (RA) (bias), precision, drift (calibration, zero), signal strength, and matrix interferences; and (2) engineering: portability, ruggedness, user-friendliness, and duty cycle. ABF-LIPS was operated in parallel with a traditional testing method (the reference method [RM]), and the results between ABF-LIPS and the RM were compared.

The primary performance criteria for the tests was the RA, or the agreement (bias) of the results reported by ABF-LIPS with the result obtained by standard U.S. Environmental Protection Agency (USEPA) methods for flue gas emission sampling and analysis. Since emissions from the test sources were typically low, spiking of the streams with an aerosol of target metals was necessary. Spiking was carried out by continuously injecting a stream of an aerosol of dissolved metal salts over the course of each test run. Both the RM sampling probes and the ABF-LIPS probe were positioned as near as possible to each other to ensure that the samples would be nearly identical. ABF-LIPS, however, analyzes samples as a “snapshot”—i.e., the instrument captures a small volume of flue gas, ignites it to a plasma state, and records the spectrographic

profile of the plasma decay. As such, a number of readings are possible during each run using ABF-LIPS (sample to sample time is several minutes [min]). The RM, however, is a time-integrated sample over the entire run (typically 2 hours); the sample is trapped on filters and in solutions for off-site analysis by a laboratory. The aerosol spiking allowed determination of target metals at each of three concentrations to determine linearity of the instrument response per the performance specification for multi-metals CEMS.

1.3 REGULATORY DRIVERS

In 1990, Congress amended Section 112 of the Clean Air Act requiring USEPA to identify and regulate all significant stationary sources that emit any of 189 HAPs. Currently, USEPA has a list of 173 source categories and is issuing regulations requiring these sources to use maximum available control technology to reduce HAP emissions. USEPA is developing regulations to limit emissions of the HAP metals from sources such as incinerators and coal-fired power plants, among others. The U.S. Department of Defense (DoD) possesses or controls many such assets which would be subject to these regulations. Continuous emissions monitoring of toxic metals has been proposed by USEPA (USEPA, 1997) and included in the Code of Federal Regulations (CFR) (40 CFR Parts 72 and 75) for use at facilities that emit HAPs. Further, CEMS are required under some USEPA regulations for either continual compliance determinations or determination of exceedances of the standards. Current approved sampling methodology is labor intensive and expensive. Furthermore, since these methods do not continuously monitor an emission, they have inherent uncertainty. Instruments such as ABF-LIPS can measure metals in real-time, but require validation using USEPA-approved methods. Further development of ABF-LIPS will be required, however, prior to additional validation testing and eventual regulatory acceptance.

1.4 DEMONSTRATION RESULTS AND IMPLICATIONS

The first test was conducted at the NADEP North Island in San Diego, California, during June 2003. A chromium (Cr) plating bath exhaust, a nickel (Ni) plating bath exhaust, and a molten metal (Kirksite) furnace were sampled. The second demonstration test was conducted at TEAD in Tooele, Utah, using the Ammunition Equipment Directorate's Ammunition Peculiar Equipment 1236M2 test furnace, a munitions deactivation test incinerator. Each source was spiked with an aerosol of three to five test metals (cadmium [Cd], Cr, lead [Pb], mercury [Hg], and Ni) at each of three concentrations (low, medium, and high). Each concentration was run in quadruplicate, resulting in a total of 12 runs for each source. The acceptance level for RA is 20% per performance specification (PS)-10 (USEPA's PS for CEMS).

The first test at NADEP produced useable data from ABF-LIPS for only one of the three sources tested—that of the molten metal furnace. The Cr and Ni plating bath source tests likely failed due to an incorrect setting of the detector exposure time. ABF-LIPS data from the molten metal furnace, in the form of emission spectra peak heights, did not correlate with the spiking levels of the three test metals (Cd, Cr, and Ni). Pearson correlation coefficients ranged from negative (anti-correlated), to weakly positive (i.e., random). In contrast, the RM results showed generally good correlation with the spiking level. The failure of these tests to produce accurate data, the primary performance objective, means that further system development and testing will be required before the instrument can be permitted for use in pollution control systems.

Modifications were made to the ABF-LIPS instrument and spiking apparatus prior to the next field tests at the TEAD. A munitions deactivation furnace was tested at TEAD in 2005, which produced data from ABF-LIPS that correlated well with the spiking levels. However, agreement with RM results was not within the PS-10 RA acceptance criteria of 20% for any of the five test metals; again, the primary performance criteria was not met. The ABF-LIPS reported emission rates were higher than the RM results by an average of 67% for the high spike concentration (per-metal ranges of 50% to 88%), and higher by 73% for the medium spike concentration (per-metal ranges of 17% to 99%). ABF-LIPS generally reported lower values for the low spike concentration; no Cd or Cr was detected, and Ni was 145% lower and Pb 1000% lower than the RM results. Hg was within 5% at the low concentration.

The TEAD RM data are suspect. Variances within the group of four runs at each concentration were high; coefficients of variation for each metal averaged 45% with a per-metal range of 27% to 81%. This suggests that the RM data are inherently flawed, and comparisons to the ABF-LIPS results are likely unreliable.

While PS-10 validation of ABF-LIPS did not meet the RA criteria, other performance objectives were met: the instrument was relatively easy to transport and set up, it operated under adverse environmental conditions without needing repairs, zero drift was within PS-10 criteria, and the analysis cycle was very short (less than 6 min).

It is unlikely the current prototype unit could be used in a real-world application, however limited, at this point. Further development of ABF-LIPS will be required prior to additional validation testing and eventual regulatory acceptance. Previous laboratory testing of the system components yielded better accuracies, suggesting that adaptation of system components to a portable, field-deployable unit used in these tests resulted in compromised data accuracy, and/or that the inherent nature of field testing with a higher degree of uncontrolled variables were likely reasons for the failed field testing. Some of these variables included the delivery of standards to the stack/flue stream, condensation of water in the instrument optics and stack/flue stream, and alignment issues due to environmental vibrations from mechanical systems and wind.

1.5 END-USER ISSUES

The major components of ABF-LIPS are commercially available instruments, including a highpower laser, an intensified charge couple array, and a spectrograph. The total cost for these three components is approximately \$120,000, which provides wide-ranging capability in detecting metal-laden aerosols in near real time. Capital costs for an ABF-LIPS system capable of measuring multi-metals (all HAP metals) is projected to be \$160,000, and annual operation and maintenance (O&M) costs are projected to be \$10,000. Assuming the useable life of an ABF-LIPS unit is 10 years, the annualized cost is \$26,000 (annual O&M + \$160,000/10). Stack monitoring of a furnace, for example, using the traditional sampling train method is estimated to cost \$40,000 annually. Thus, ABF-LIPS would save \$14,000 per year per source. Savings would be multiplicative at facilities where a single ABF-LIPS unit could be used portably on multiple sources; as is the case at many DoD installations. In addition, ABF-LIPS is the only method that will provide continuous emission monitoring, an expected requirement of upcoming regulations.

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2.0 INTRODUCTION

2.1 BACKGROUND

CEMS provide an effective means for monitoring the level of HAPs in real time. CEMS also ensure that the maximum achievable control technology is performing as specified. HAPs include the following metals: arsenic (As), antimony (Sb), barium (Ba), beryllium (Be), Cd, Cr, cobalt (Co), Pb, manganese (Mn), Hg, Ni, selenium (Se), silver (Ag), and thallium (Tl). These metals are commonly associated with airborne particulate matter and are emitted from various industrial and military activities, such as power generation, industrial manufacturing processes (e.g., nuclear and munitions), welding, plating, munitions detonation or burning, and waste combustion. All of these activities are important to the missions of the DoD. With increasing scrutiny of land use, encroachment, and environmental regulations, DoD installations in the United States have faced tremendous pressure on environmental quality including air quality management, control, and emissions reduction. An effective emissions control and reduction program requires monitoring that is real time and on line.

Currently, metals in flue gas emissions are measured using a sampling train to collect a time-integrated sample over a 1-hour (hr) period for medium to high concentration levels, and a 2-hr period for low concentrations. The resulting samples are delivered to an analytical laboratory and analyzed by a variety of traditional methods including instrumental neutron activation analysis, x-ray fluorescence (XRF), and inductively coupled plasma (ICP). Results are reported in terms of the elemental composition associated with the particulate matter collected on each sample filter from the sampling train. These procedures are very time consuming and prone to errors in particle sampling, filter handling and storage, and analytical errors. The traditional sampling procedures and analytical methods also do not provide essential data needed to support anticipated regulatory requirements for continuous emission monitoring, nor do they provide information for real-time decision making or engineering process control.

Facilities that do not have CEMS typically rely on restrictive operating conditions to promote compliant operations. Currently, there are two commercially-available CEMS for metals, the Trace AIR system, marketed by Thermal Jarrell Ash, and the x-ray continuous emission monitoring system (XCEMS) by Cooper Environmental, Inc., but the units are large, non-portable, generally require a long sampling line, and are relatively costly.

The need for CEMS is due in large part to regulations and improved process control. In 1990, Congress amended Section 112 of the Clean Air Act requiring USEPA to identify and regulate all significant stationary sources that emit any of 189 HAPs. Currently, USEPA has a list of 173 source categories and is issuing regulations requiring these sources to use maximum available control technology to reduce HAP emissions. USEPA is developing regulations to limit emissions of the HAP metals from sources such as incinerators and coal-fired power plants. The proposed limits for hazardous waste incinerators for metals are shown in Table 1. The DoD possesses or controls many such assets which would be subject to these regulations. Continuous emissions monitoring of toxic metals has been proposed by USEPA (USEPA, 1997) and included in the CFR (40 CFR Parts 72 and 75) for use at facilities that emit HAPs. Further, CEMS are required under some USEPA regulations for either continual compliance determinations or determination of exceedances of the standards. Current approved sampling

methodology is labor intensive and expensive, and since these methods do not continuously monitor an emission, they have inherent uncertainty. Instruments such as ABF-LIPS can measure metals in real time, but require validation using USEPA-approved methods. This will also allow for better process control; current processes must be operated somewhat conservatively due to the uncertainty in actual emissions for various conditions.

Table 1. Proposed USEPA Hazardous Waste Incineration Standards, Tier III Reference Air Concentrations

Carcinogenic Metals	µg/m³ (annual limit)	Non-Carcinogenic Metals	µg/m³ (annual limit)
As	2.3×10^{-3}	Sb	0.3
Be	4.1×10^{-3}	Ba	50
Cd	5.5×10^{-3}	Pb	0.09
Cr	8.3×10^{-4}	Hg	0.3
		Ag	3
		Tl	0.3

(40 CFR Parts 260, 261, 264 and 270, Federal Register Volume 55, No. 82, April 27, 1990)

µg = microgram

2.2 TECHNOLOGY DEVELOPMENT AND APPLICATION

Measurement of metal HAPs using laser-induced plasma spectrometry has been adapted to a field portable instrument, ABF-LIPS. The aerosol beam focusing capability improves the detection and sensitivity of traditional LIPS by aerodynamically focusing aerosol particles to a point, increasing the local aerosol concentration and significantly improving the signal-to-noise ratio. The principle of operation of ABF-LIPS is a pulsed laser beam tightly focused onto an aerosol sample to ignite a plasma, which breaks down all compounds to their elemental composition. The elements in the plasma volume are vaporized, resulting in an unstable, excited state. When the atoms return from the plasma-excited state to ground, they release light at element-specific wavelengths that can be observed using time-resolved spectroscopy. The wavelengths of the emission spectra correspond to a particular element, and the amplitudes of the peaks correspond to the mass of that element. The ABF-LIPS instrument, because of its portability, can be mounted at an emission source and requires no long sampling line, which virtually eliminates sample loss. Development of ABF-LIPS has been carried out at ORNL with funding from the Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP).

ABF-LIPS was developed under SERDP during fiscal years 1997-2000. ABF-LIPS addresses a number of the shortcomings associated with traditional stack monitoring and commercially-available metals CEMS. The present instrument design comprises physical dimensions of 24 in (L) × 24 in (W) × 24 in (H) and a weight of about 50 pounds. Unlike the Trace AIR metals CEMS, the ABF-LIPS system has aerosol-focusing capability, which significantly improves measurement sensitivity. ABF-LIPS can also be used in place of stack gas sampling trains for sources that require periodic stack gas emission measurements. In addition, multiple measurements can be taken and averaged to determine statistical confidence since each measurement can be taken in as little as 2 min.

2.3 PROCESS DESCRIPTION

The key to successful measurement of the chemical composition of aerosols is the effective delivery of the aerosol, without loss and with as little disturbance as possible, to the laser focal volume. Most spectroscopic techniques lack an aerosol-sampling module and therefore do not work well with aerosol samples. ORNL developed a novel integration of aerosol beam-focusing technology and time-resolved laser-induced plasma spectroscopy (Cheng, 2000; Cheng, 2001; Cheng et al., 2002; Cheng, 2003; Cheng and Vannice, 2003). This technique led to the development of a compact aerosol spectrometer (ABF-LIPS) which is field portable and has high analytical precision with greater sensitivity than traditional spectroscopic techniques. ABF-LIPS measurement technology has wide-ranging applications and would provide a high return on investment due largely to cost savings compared to traditional monitoring. In addition to monitoring emissions of toxic metals from stacks, the technology can be used in area detection, for instance to measure Be aerosol in a nuclear manufacturing facility (Cheng et al., 2004; Cheng and Smithwick, 2005).

The ABF-LIPS technique improves the detection and sensitivity of traditional LIPS (also known as laser-induced breakdown spectroscopy [LIBS]) by aerodynamically focusing aerosol particles to a point, increasing the local aerosol concentration and significantly improving the signal-to-noise ratio. In ABF-LIPS, a pulsed laser beam is tightly focused onto an aerosol sample to ignite a plasma, which breaks down all compounds to their elemental composition. All elements in the plasma volume are vaporized, and the atoms are energized to an unstable, excited state. When the atoms return from the plasma-excited state to ground, they release light at element-specific wavelengths that can be observed using time-resolved spectroscopy. The characteristic emission spectra wavelengths correspond to a particular element, and the amplitude of the peaks correspond to the mass and concentration of that element. The ICP CEMS (e.g., Trace Air) does not employ time-resolved analysis nor does it use an aerosol beam-focusing technique to provide a precise delivery of aerosol mass to the plasma volume for sensitive detection. ABF-LIPS has been awarded U.S. Patent No. 6,359,687. A schematic of ABF-LIPS is provided in Figure 1. Figures 2 and 3 illustrate the principles of aerosol focusing and concentration of particles.

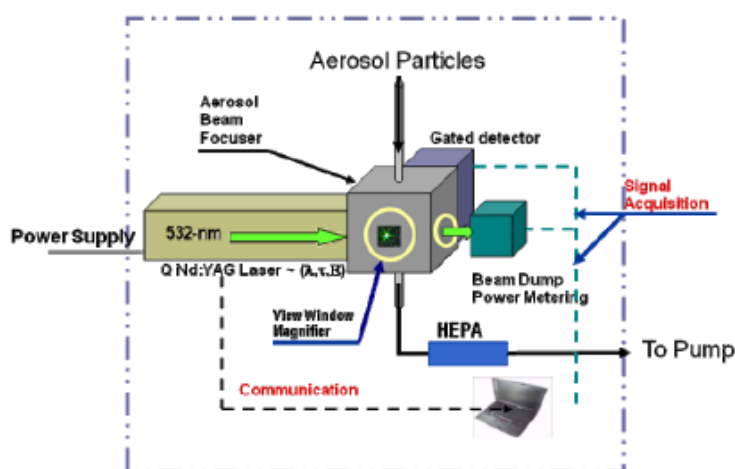


Figure 1. Schematic of ABF-LIPS.

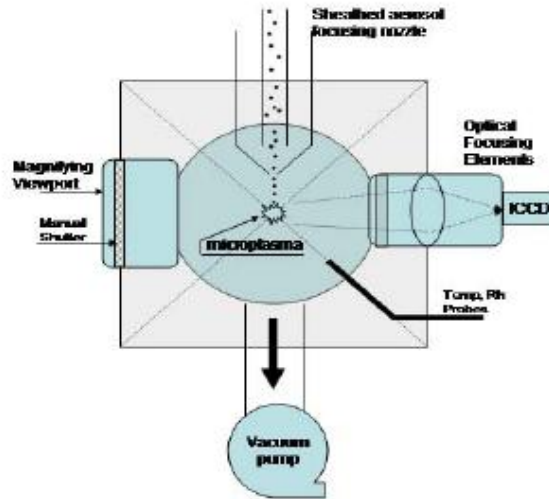


Figure 2. Schematic of aerosol focusing process.

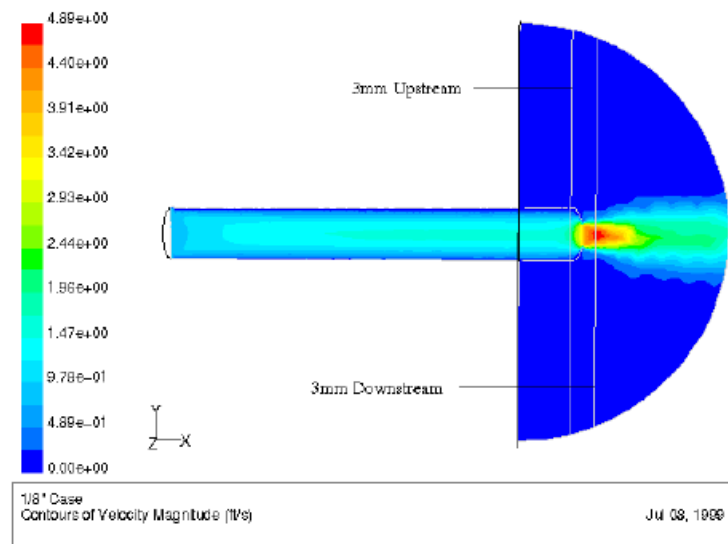


Figure 3. Focusing simulation by computational fluid dynamic modeling.

In the ABF-LIPS process, a laser ignites the plasma and the resulting emissions spectra are passed through an Echelette grating so that the individual wavelengths can be measured by the image sensor. The spectral window created by the grating ranges from 180 to 900 nanometers (nm). Multiple orders of diffraction from the Echelette grating are separated by a cross-dispersion prism before they are imaged on the image sensor, an intensified charge-coupled device (ICCD). This allows for high-resolution detection across the entire wavelength range of the ICCD, obviating the requirement to scan a grating. The detector chip is a large-scale integrated circuit containing hundreds of thousands of photo-sites (pixels), which convert light energy to electronic signals. The ICCD effectively becomes an array of many thousands of pixels, which then sample each wavelength present. The ICCD is coupled through fiber optics with an image intensifier for low light level pickup, increasing the sensitivity and signal-to-noise

ratio of the detector. The ICCD has very high sensitivity and nanosecond time resolution. The integrated spectrometer (Echelette and ICCD) has no moving parts, making it a good candidate for field measurement. The spectra from each sample are stored on a laptop computer and processing software determines the elemental composition and concentration of the aerosol sample.

PS-10 for CEMS requires that RA be within 20% of the mean of the RM. Instrument drift from the calibration standard and the zero value must not exceed 5% (values measured daily over 7 days) per PS-10.

TEAD required setup of about 1 hr and each analysis cycle required minimal input (several keystrokes) to the controlling notebook computer. The final, marketable instrument will have a self-contained, menu-driven controller with built-in display. Training of personnel can be accomplished in the field in less than a half-day, including basic trouble-shooting. Because of the portability of the unit, advanced trouble-shooting could be performed by economically shipping the unit to the factory or repair facility.

2.4 PREVIOUS TESTING

The ABF-LIPS technology was initially tested in the laboratory from 1998 to 2000 using synthetic aerosol particles. The particles were produced from prepared solutions consisting of known amounts of single and/or multiple elements. Elements of interest during the laboratory tests included Pb, Cr, Ni, Hg, zinc (Zn), copper (Cu), carbon (C), iron (Fe), aluminum (Al), and sulfur (S). Aerosols were generated using techniques such as vibrating orifice aerosol generation, vaporization-condensation, electrospray, and atomization-nebulization methods. A variety of techniques were used so that a wide range of particle sizes ranging from a few nanometers to a few micrometers could be generated. The generated particles were dried and transferred into a flow reactor which also served as an aerosol sampling manifold.

The technology was further developed and subsequently refined in 2000. A field-portable unit, shown in Figure 4, was assembled on a wheeled platform. This represented the second-generation of ABF-LIPS. In this unit, a small Q-switched Nd:YAG laser emitting green light (at 532-nm wavelength) was used as the excitation energy source. A computer-driven grating coupled to an ICCD array was used for the time-resolved plasma emission spectroscopy. The aerosol-focusing cell was mounted directly to the light entrance of the grating box (spectrograph). Collimating lenses were placed between the cell and the spectrograph to align the incident light with the grating slits, housed in a cage to prevent misalignment during transportation in the field. The excess laser energy was discarded to a beam dump at the other end of the cell. The aerosol particles were drawn into the focusing cell by a piston pump operated at a flow rate approximately 2.5 L/min, and the focusing position was 2 mm from the nozzle exit.



Figure 4. ABF-LIPS prototype.

The prototype ABF-LIPS had undergone previous field-testing between 2000 and 2002 using particles from a diesel engine at the National Transportation Research Center at ORNL in Knoxville, Tennessee, and a chemical disrupter located at the Eastman Chemical Company (Eastman) in Kingsport, Tennessee (Cheng and Vannice, 2003; Cheng, 2003). These sources included a diesel engine research facility where Cr, vanadium, Cu, and platinum were of interest, and an industrial waste incinerator at Eastman. The emissions from one of the Eastman kilns were measured and metal-laden aerosol particles were also spiked into the emission flue gas. The elements of interest in the Eastman test included Cr, Hg, and Be. The Eastman test results were presented at the Air and Waste Management Association national meeting in San Diego, California, in June 2003. Cheng (2003) detailed the test results from the Eastman campaign in 2002.

2.5 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

ABF-LIPS technology was designed primarily for aerosol measurement, particularly for measuring metal-laden aerosols. ABF-LIPS has several advantages over current methods for measuring aerosol metals. These include: (1) more effective aerosol sampling and transport than current instruments; (2) better analytical performance criteria (better precision, accuracy, and linear dynamic range; (3) ease of operation (no filter, no preparation, and much less labor intensive); (4) no analytical waste generated; (5) faster turnaround time (near real-time, typically 6 min) compared to days and weeks for traditional filter sampling; and (6) versatile design that potentially facilitates user-specific modifications.

The limitations of the current ABF-LIPS technology include interferences from the background matrix, which can be significant when a weak signal (low concentration) is present. Similarly, when small particles (on the order of tens of a nanometer) are to be analyzed, interference appears to be significant, leading to a weak signal-to-noise ratio. The excitation source is limited to a few choices since the requirements for air and aerosol breakdown are much higher than that for solid samples. However, in 2003, project researchers developed a new excitation source which is very effective in analyzing large (tens of micrometers) and small (tens of nanometer) aerosol particles. The new technique is archived for Department of Energy intellectual property and is currently being considered by ORNL for patent application. Other limitations of LIPS

include the scarcity of commercially-available standards, lower detection limits than those of solution-based methods, and the possibility of eye damage due the high-energy laser.

Table 2 provides a summary comparison of ABF-LIPS with other commercial and known instruments that measure metal emissions. With the exception of the TraceAir and XCEMS, these instruments are not available as CEMS—most are suitable for laboratory applications only. The TraceAir (Thermo Jarrel-Ash) is a large (trailer-size), costly system requiring frequent maintenance and supply of consumables. The XCEMS (Cooper Environmental, Inc.) is much smaller than the TraceAir but is not portable. The XCEMS has a minimum detection limit of 1 to 3 $\mu\text{g}/\text{dry standard cubic meter (DSCM)}$ and its detector is non-destructive, so the same sample material from the filter paper can be sent to a laboratory for verification testing. ABF-LIPS, because of its aerosol-focusing capability, has been demonstrated in the laboratory to attain detection limits of 1 $\mu\text{g}/\text{DSCM}$ and below. Maximum detection limits for the ABF-LIPS technique could be increased by lowering the gain of the detector. This would virtually allow for an unlimited maximum detection level (at the expense of the minimum detection level), but will require further development and additional expense of the production unit. Swamping of the detector by other elements, however, intrinsically limits the maximum and minimum detection levels of the instrument. The ABF-LIPS detector is destructive so additional, parallel samples have to be collected for verification testing. Since the XCEMS and ABF-LIPS use different detectors, they are more or less sensitive to various matrix interferences, and therefore one system may be more suitable for a particular application than the other.

Table 2. Comparison of ABF-LIPS with other metals emission monitors.

Monitor Feature	ABF-LIPS	TraceAir	XRF	SpectroLaser	OceanOptics LIBS2000+	ADA	SEA	XCEMS
Excitation source	Nd:YAG laser	ICP	X-Ray	Nd:YAG laser	Nd:YAG laser	Nd:YAG laser	N/A	SRF
Electrical enhancement	Yes	No	No	No	No	No	No	
Spectrograph	Echelle	Echelle	Echelle	Czerny-Turner	Czerny-Turner	Optical filter	N/A	
Detector	ICCD	CCD		CCD	CCD	PMT/Photodiode	N/A	
No of detectors	1	1	1	4	1	1	N/A	
Gated detection	Yes	No	No	No	No	No	N/A	
Wavelength (nm) covered	180-900			180-800	200-980	Be only, 1 element	N/A	
Aerosol focusing	Yes	No	No	No	No	No	No	No
Sample preparation	No	No	No	Yes	Yes	Yes	N/A	Yes
Spatial resolution	Yes	No	No	No	No	Yes	N/A	
Waste produced	No	No	No	Yes	Yes	Yes	N/A	Yes
Consumables	No	Yes	No	Yes	Yes	Yes	N/A	Yes
Field deployable	Yes	Yes	Yes	Bench-top	Bench-Top	Yes	Possible	Yes
Operable by one person	Yes	No	No	N/A for field operation	N/A for field operation	Possible	N/A	Yes
Size of analysis head module (H×W×D)	24 in×18 in×9 in, 45 lbs	Trailer	24 in×36 in×48 in, 400 lbs	15 in×29 in×12 in, 132 lbs	19 in×19 in×13.8 in, weight unknown	16 in×20 in×28.3 in, 43 lbs	On a wheeled platform	72 in×36 in×36 in
Cost	\$90-\$150,000		\$275,000		~ \$60,000			~\$250,000

XRF=x-ray fluorescence

3.0 DEMONSTRATION DESIGN

The objectives of this ESTCP project are to:

- To field-validate ABF-LIPS performance by collecting data under real-world conditions and comparing the data to data obtained simultaneously by a USEPA-certified standard RM. The performance parameters include:
 - RA
 - Precision
 - Span, zero, and drift
 - Signal strength
 - Response time
- To conduct field tests at selected military facilities under various environmental and source conditions. Variable conditions included source type, humidity, temperature, and background or interference gas composition.
- To collect field-specific performance data including duty cycle, temperature and vibration tolerance, ease of transportation and setup, and climate influences. These data will aid in improving the re-design and packaging of a commercial field-portable platform system.
- To collect cost data for ABF-LIPS to compare to other methods.

3.1 PERFORMANCE OBJECTIVES

The performance objectives of this demonstration are to obtain data under real-world conditions to complement laboratory data and previous field testing. The performance criteria include (1) analytical performance: RA (bias), precision, drift (calibration, zero), signal strength, and matrix interferences; and (2) engineering: portability, ruggedness, user-friendliness, and duty cycle. The analytical performance criteria are quantitative dimensions and the engineering criteria are qualitative here. Table 3 further describes the performance criteria, acceptance criteria requirements, procedures and action, and notes.

Table 3. Data quality and quality assurance objectives.

QA Indicator	Description	Requirement	Action	Notes
Relative accuracy (bias)	Result compared to reference method	+/-20%	Nine data pairs minimum at three levels	12 data pairs at three levels will be collected
Two or more metals	Sb, As, Ba, Be, Cd, Co, Cr, Pb, Hg, Mn, Ni, Se, Ag, Tl	Two metals minimum	Instrument can be used as a CEM only for metals that are tested	Cd, Cr, Ni, Pb, and Hg will be monitored in this field test
Calibration drift	Difference in output of reference value after stated period of operation	Within 5%, measured once each day for 7 consecutive days	Measured once at the beginning and end of each test day using the medium concentration spike under regular test operating conditions	Instrument will be checked at the beginning and end of each test day
Zero drift	Difference in output with zero input after stated period of operation	Within 5%, measured once each day for 7 consecutive days	Measured once at the beginning and end of each test day using ambient air	Instrument will be checked at the beginning and end of each test day
Response time	Amount of time instrument requires to respond to a steady state reading at least 95% of maximum	Less than 2 min	See note	For ABF-LIPS this is a near-instantaneous figure (milliseconds)
Calibration standard	A known amount of metal(s) delivered to the CEMS to determine response and drift	Performed at +/-20% of the applicable emission standard for each metal	Performed at the beginning (and end, for calibration drift [CD]) of each day using the medium concentration spike under regular test conditions	
Measurement location	Probe inlet should be in location with minimal turbulence or flow disturbance	At least 8 equivalent diameter distances downstream of any control device, bend, spike introduction, etc.	Will use existing ports	Existing ports are all within minimum requirement
RM measurement and traverse points	Location at least 8 equivalent diameters beyond flow disturbances, spike introduction, etc.	At least 8 equivalent diameter distances downstream of any control device, bend, spike introduction, etc.	Will comply with appropriate regulations (see note)	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.

Table 3. Data quality and quality assurance objectives (continued).

QA Indicator	Description	Requirement	Action	Notes
Practical limit of quantitation	Minimum detection level in this application	10× the standard deviation (SD) at the blank level	Measure zero or ambient air and calculate SD of mean	ABF LIPS ambient air produced no photon counts
Capability in various environments and conditions	Exposure to various climates and source operating conditions should not impact data quality	Performance within acceptable criteria in varying weather conditions	Perform measurements in varying weather conditions in outdoor locations within acceptable accuracy criteria	Accuracy should be within acceptance criteria in hot and cold ambient temperatures typical of test locations. If temperature extremes affect performance, climate controlled housings/buildings may be required for deployment.
Ruggedness, user-friendliness, ease of setup	Instrument should survive transport to site, vibration or shock during deployment, etc. Time required for setup, operation learning, and troubleshooting should not exceed several days.	Ruggedness: Performance should be unaffected by transportation, setup and day-to-day operation at site. User- friendliness/ setup ease: New users should become proficient within several days of training and operation and instrument should not break down.	Transport and setup times will be noted. New users will be trained to operate equipment during tests and will operate instrument if possible.	

USEPA PS-10 (Appendix B) is the final rule proposal specification for assessing the acceptability of multi-metal CEMS in terms of quality assurance objectives. PS-10 has been adopted in these demonstrations to assess the performance of ABF-LIPS. The performance criteria listed in PS-10 include the following:

- RA.** The RA of the CEMS must be no greater than 20% of the mean value of the RM test data in terms of units of the emission standard for each metal, or 10% of the applicable standard, whichever is greater. Obtain a minimum of three pairs of CEMS and RM measurements for each metal required and at each level required (see Section 7.1 of PS-10, included as Appendix B). 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.

According to PS-10, RA is calculated as follows:

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

where $\bar{d}$ is equal to the arithmetic mean of the difference d , of the paired CEMS and RM data set, SD is the SD of the data set, n is the number of measurements in the data set, $\bar{R}$ is the average of the reference measurements, and $t_{0.975}$ is the t -value at 2.5% error confidence as listed in Table 1 of PS-10.

- Testing of ABF-LIPS made use of 12 test runs at each source/test location. The 12 test runs included four test runs at each of three spiked metals concentrations (low, medium, and high concentration). The metals included Cd, Cr, and Ni for the field test at NADEP. Pb and Hg were added as for the field test at the munitions deactivation furnace (DF) at TEAD.
- **CD.** The CEMS design must allow the determination of CD 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% of the emission standard for each metal. The calibration shall be performed at a point equal to 80 to 120% of the applicable emission standard for each metal.
- **Zero Drift.** The CEMS design must allow the determination of CD 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% of the emission limit value). The CEMS zero point for each metal shall not drift by more than 5% of the emission standard for that metal. The prescribed period is once each day for 7 consecutive days.

3.2 SELECTION OF TEST FACILITIES

Two facilities were selected for demonstration testing. The first test was conducted at the NADEP North Island in San Diego, California, during June 2003 at a metal plating facility and at a molten metal furnace. The NADEP plating facility served as the low temperature test site, and the furnace served as a mid-temperature source. The second demonstration test was conducted at TEAD in Tooele, Utah, using the Ammunition Equipment Directorate's Ammunition Peculiar Equipment (APE) 1236M2 test furnace, a munitions deactivation test furnace, which served as the high temperature test site. The first field test attempt at TEAD during October 2004 was aborted due to freezing weather and blowing snow. The second field test at TEAD was completed during September 2005. The test facilities for NADEP and TEAD are further described in the following subsections.

3.2.1 Test Facility Selection – NADEP

NADEP, North Island, has over 80 years of service to the fleet. It provides a wide range of engineering, calibration, manufacturing, overhaul and repair services performed on F/A-18, E-2, C-2, H-60, and S-3 aircraft and on ships. The Primary Standards Laboratory provides primary

calibration standards for the Navy and other agencies of the DoD throughout the United States and overseas. A 50,000 square foot structure, built to meet the Navy's evolving aviation requirements, houses the Navy Primary Standards and Materials Engineering Laboratories.

NADEP performs metal finishing operations and includes Cd, chrome, and Ni lines. Cr coatings provide excellent wear resistance and corrosion protection. Hard chrome coatings are thick layers of Cr used to give a part extra wear resistance. Ni coatings are used to improve corrosion resistance, wear resistance, and magnetic characteristics. Ni is considered to be very flexible in metal plating because the properties of Ni coatings can be controlled and varied relatively easily.

The low temperature demonstration test was conducted at a plating facility at NADEP on June 15-18, 2003. Two plating bath sources were tested: a hard chrome plating line and an electroless Ni line. A mid-temperature source was also tested: a molten metal furnace used to heat the metal alloy Kirksite to a molten state (Kirksite is the name of a moderate-strength metal alloy used to produce non-stressed parts, molds, and dies). Sampling locations on the electroless Ni and chrome plating line were located following emission control devices; the Kirksite furnace sampling location was prior to emission control devices. The Kirksite furnace has no emissions control device.

3.2.1.1 Chrome Plating

NADEP conducts metal finishing operations that utilize five hard chrome plating tanks located in Building 472. The facility typically plates 3 to 5 million amp-hours per year and is identified as a Small Hard Cr Electroplating Facility by the San Diego Air Pollution Control District.

The hard chrome plating tanks are part of plating Line #7, which includes a maskant soak tank and tanks P7-4, P7-5, P7-8, P7-9, P7-12, and P7-13. Tank P7-9 is a sulfuric acid activation tank, and the remaining five tanks are hard chrome plating tanks. Emissions from all seven tanks are collected by 3-inch high slot type hoods on the back side of each tank, which are joined to form one central duct that is routed to the control system outside the building at ground level. The front of each tank is equipped with a push air header to provide a slipstream of air to assist in collecting the mist formed during plating. The chrome plating tanks and hood exhaust ducting are shown in Figure 5. Outside the building, the emission stream is divided into two parts before entering parallel Enforcer III composite mesh pad systems which are manufactured by MAPCO and exhausted through 36-inch diameter ducts that join at roof level to a single 49.5-in diameter horizontal duct before entering a 100-horsepower (hp) blower and exiting to the atmosphere via a stack.



Figure 5. Cr plating bath operation at NADEP.

The Enforcer III is equipped with four separate mesh pads, each with its own washdown system consisting of a series of spray nozzles and a control valve. The 100-hp blower induces the draft in the system and exhausts it to atmosphere. The second (Stage 3), third (Stage 4), and fourth (Stage 5) mesh pads are washed down periodically with purified water for about 15 seconds (sec). The approximate wash cycle intervals are every 4 hours for the second mesh pad, every 6 hours for the third mesh pad, and every 24 hours for the fourth mesh pad. The washdown from these three mesh pads drains into a common tank, which supplies the recirculated water to wash down the first mesh pad of each Enforcer III. The first mesh pad (Stage 1) acts as an evaporator and is washed down frequently (every 30 min for 30 sec) and is followed by a section of chevron blades (Stage 2) which demist the air stream and protect the latter stages from contaminated moisture. Washdown from the latter stages drains through the chevrons for cleaning. Test ports are installed on the exhaust stack approximately 8 duct diameters from the nearest upstream elbows and 2 duct diameters from the nearest downstream disturbance as shown in Figure 6. The exhaust stack diameter is 49.5 in. Two existing test ports at right angles accommodate dual train RM (USEPA Method 29) probes; a third test port was installed (several in upstream of the existing two) to accommodate the ABF-LIPS probe. Heavy metals spiking was performed at the exhaust of each Enforcer III system using two nebulizers (one on each duct) just before the ducts joined at roof level. The nebulizers were set to deliver a constant flow of heavy metals solution using each of three separate stock solutions (low, medium, and high concentrations).



Figure 6. Sampling port on Cr plating bath exhaust on roof of building at NADEP.

3.2.1.2 Electroless Ni

Electroless Ni produces an alloy with distinct properties. Electroless Ni is a process that deposits a uniform thickness of Ni onto the parts by chemical reduction. In an aqueous solution containing hypophosphite, Ni ions reduce to Ni-metal, which coats the substrate surface. This allows complex-shaped parts to be plated evenly and completely. These properties have made electroless Ni very useful in a broad range of functional applications that take advantage of the hardness, lubricity, corrosion resistance, electrical and magnetic properties of electroless Ni.

The electroless Ni tanks are part of Line #2, which includes tanks P2-9A, P2-B, P2-10, P2-11, P2-12, and P2-13 in Building 472. Emissions from the Ni tanks are collected by 3-inch slot type hoods on the back side of each tank. The hoods are manifolded together beneath the floor. The front of each tank is equipped with a push air header to provide a slipstream of air to assist in collecting the mist during plating. The emission stream is vented to a demister and a 20-hp blower prior to discharge to the atmosphere (Figure 7). The source tests on the Ni tanks were conducted on the exhaust of the mist eliminator just below roof level. Metal spiking was performed at the exit of the mist eliminator.



Figure 7. Electroless Ni plating bath exhaust stack on roof of building at NADEP.

3.2.1.3 Kirksite Furnace

NADEP conducts casting operations in Building 65, which utilize a furnace for the melting of a Zn-base alloy known as Kirksite. Kirksite is a moderate strength Zn-base alloy developed primarily as a forming tool alloy. Dies cast from the Kirksite foundry provide low-cost tooling because the alloy can be accurately cast, requiring a minimum of finishing. In addition, Kirksite has been used as a general purpose casting alloy for non-stressed components. Due to the alloy's fluidity and low melting temperature, casting temperatures are low, 800 to 850 degrees Fahrenheit (°F). The alloy is normally cast in permanent, plaster or sand molds. The Kirksite is then machined and polished. A drop hammer, an air operated machine capable of high velocity impacts, is then used to form the aircraft parts. The furnace is enclosed on three sides and hooded on the top to collect the emissions from the furnace. The hood is vented at the back to a blower that exhausts the fumes out the side of the building and up beyond the roof to the atmosphere. A photograph of the Kirksite melting pot and hood are included as Figure 8.



Figure 8. Kirksite furnace melting pot in hood at NADEP.

The source tests on the Kirksite furnace were conducted on the exhaust to atmosphere at roof level. Metal spiking was performed at the suction side of the blower.

3.2.2 Test Facility Selection – TEAD

TEAD is a Tier 1 active joint ammunition storage site located on 23,610 acres 1-hr west of Salt Lake City, Utah. TEAD is responsible for shipping, storing, receiving, inspecting, demilitarization, and maintaining training and war reserve conventional ammunition and APE. TEAD has a test facility which includes a prototype APE 1236M2 DF, flashing furnace, and a number of structures where certain APE are developed, tested, and evaluated. The furnaces and their ancillary equipment are used as a test facility to evaluate the efficiencies of air pollution control technologies and determine proper feed rate conditions for munitions items. The only munitions fed into the APE 1236M2 prototype DF are those necessary to conduct tests.

The second field test of ABF-LIPS was conducted at TEAD's APE 1236M2, serving as the high-temperature test facility. The APE 1236M2 DF system, shown in Figure 9, consists of a main control panel, a conveyor feed/discharge system, a rotary furnace, a cyclone separator, an afterburner, CEMS, a waste feed rate monitoring system (WFRMS), a high temperature cast ceramic filters bag house, a high temperature draft fan, and an exhaust stack. A number of sensors (temperature, gas flow, pressure differential, combustion gases, etc.) are used to monitor operating conditions at various points in the system. Signals from these sensors are monitored and compared to preset operating standards.



Figure 9. APE 1232M2 prototype munitions deactivation furnace demonstration site, TEAD, Tooele, Utah.

A detailed description of system components follows:

Main Control Panel – The main control panel contains various pieces of control equipment to monitor and control the furnace operation. Process controllers are used to control the rotary furnace feed end temperature, negative pressure in the furnace, and the afterburner temperature. A multi-point digital recorder is used to record process parameters. Logic control for the furnace is by a programmable logic controller (PLC). The PLC controls the motor starters, the WFRMS, safety interlocks and alarms.

Continuous Emission Monitoring System – The CEMS measures carbon monoxide (CO) and oxygen (O₂) in the exhaust stack. The CEMS includes the following: sample extraction ports, refrigerated condenser, sample pump, filters, and flow meters. The sample extraction port is located in the exhaust stack approximately 20 feet above ground. The CEMS includes automatic calibration, which allows the monitors to be calibrated periodically with operation intervention. The CO monitor is a non-dispersive infrared analyzer with 0 to 200 parts per million (ppm) and 0 to 3000 ppm dual range capability. The output from the CO monitor is corrected to 7% O₂ using data from the O₂ CEMS.

Waste Feed Rate Monitoring System – The WFRMS controls the furnace feed rate. The WFRMS consists of a precision explosive proof scale, a push-off box, and a slide serial communication cable. The PLC verifies that the weight is less than or equal to the established limit acceptable for the item, the push-off box pushes the ammunition item onto the slide chute, which is over the primary feed conveyor. The WFRMS is capable of cycling every 15 sec.

Conveyor Feed System – The waste feed conveyor transports the munitions from the WFRMS through the concrete wall into the barricade area. The ammunition is then deposited into the rotary furnace feed chute.

Rotary Furnace – The rotary furnace is designed to ignite the ammunition items and effectively incinerate the reactive components from the metallic shells. The heat to ignite the ammunition is initially provided by fuel oil firing countercurrent to the movement of the ammunition through the rotary furnace. Combustion gases and the entrained ash exit the furnace adjacent to the feed chute. Non-entrained ash and the metal components of the ammunition are discharged at the burner end of the rotary furnace. The ammunition is propelled through the 20 foot (ft) long, 30.5-in diameter retort toward the burner end by spiral flights. As the ammunition approaches the flame, it either detonates or burns freely, depending on the ammunition characteristics. Thick cast steel walls contain high order detonations. Feed rates, residence times, and operating parameters have been established for each ammunition item by controlled testing. The rotary furnace is equipped with a Hauck 783 proportioning burner located at the discharge end. The burner has a capacity of 3 million British thermal units (BTU)/hr and a nominal turndown ratio of 4:1. The feed end temperature of the furnace ranges between 350 to 450°F, while the discharge end ranges from 800 to 1100°F during normal operation. The rotary furnace is operated under a slight negative pressure and was operated at 1.4 revolutions per minute (rpm) during ABF-LIPS testing.

Furnace Shroud – A metal shroud that completely encloses the retort controls fugitive emissions from the furnace. The draft fan is used to maintain negative pressure at the free end of the furnace. The retort combustion air fan draws air from the area beneath the retort shroud, creating a negative pressure. The combustion air blower creates a negative pressure inside the shroud that pulls any fugitive emissions through the blower and discharges them into the furnace via the furnace burner.

Cyclone – Large particles from the gas stream are removed by the cyclone. The cyclone (Ducon Environmental Model 700/130, size 163) has a 90 to 95% removal at clock-wise rotation, with inlet and outlet ducts at 90° separation. Particles are removed from the cyclone at the bottom by a double tipping valve. The valve has two gates which are motor driven. The gates open alternately so that only one gate is open at any given time, thus maintaining the negative pressure.

Afterburner – The afterburner (AP1204 made by Southern Technologies and equipped with an 8.7 MM BTU/hr diesel fired burner) is designed to raise the temperature of the exhaust gases exiting the kiln. This elevated temperature, and the added residence time, enhances the completeness of combustion of the explosives. The afterburner is capable of heating 4000 standard cubic feet per minute (scfm) of flue gas from 350 to 450°F to 1400 to 1600°F with a minimum flue gas residence time of 2 sec. A diesel-fuel burner with a propane pilot ignition system heats the afterburner. The afterburner is equipped with a Hauck WR0164 wide range burner with a capacity of 8.7 million BTU/hr and a nominal turndown ratio of 10:1.

Discharge Conveyor – The solid waste exits the furnace by the discharge conveyor located at the discharge/burner end. The solid waste is typically comprised of the metal casings, melted Pb projectiles, and residual ash. The low end of the discharge conveyor is located underneath the

discharge burner end of the rotary furnace. The high end of the conveyor passes through the barricade wall and deposits the waste into containers.

High Temperature Cast Ceramic Filter Bag House – The bag house is a high temperature cast ceramic collector, used for final particulate cleansing of the gas stream. The flue gas from the afterburner is transported to the bag house by a 120 ft by 30-in diameter stainless steel ducting. The ducting is long enough to produce a temperature drop from 1600°F at the exit of the afterburner to 1000°F prior to entering the bag house. The bag house, made by JT Systems, contains 154 cerafil ceramic candles which are 10 ft by 5.75-in in diameter. This results in a total filter area of 2330 square ft with a filtration velocity of 4.97 ft per sec. The bag house operates with a delta pressure range of 0.5- to 6.0-in of water column. The particles settle into the hopper below and are exhausted through a double tipping gate valve into a sealed 55-gallon drum while maintaining an air seal on the bag house assembly.

High Temperature Draft Fan – The gas stream is pulled through the air pollution control system by an induced draft fan. The fan is capable of pulling 6700 scfm at a draft (negative pressure) of 30-in of water column.

Exhaust Stack – The A36 C steel, circular exhaust stack is approximately 30 ft high (34 ft with extension) and has a nominal inside diameter (ID) of 19.625 in. A photograph of the exhaust stack is included as Figure 10. A system schematic with injection and sampling locations is shown in Appendix E.

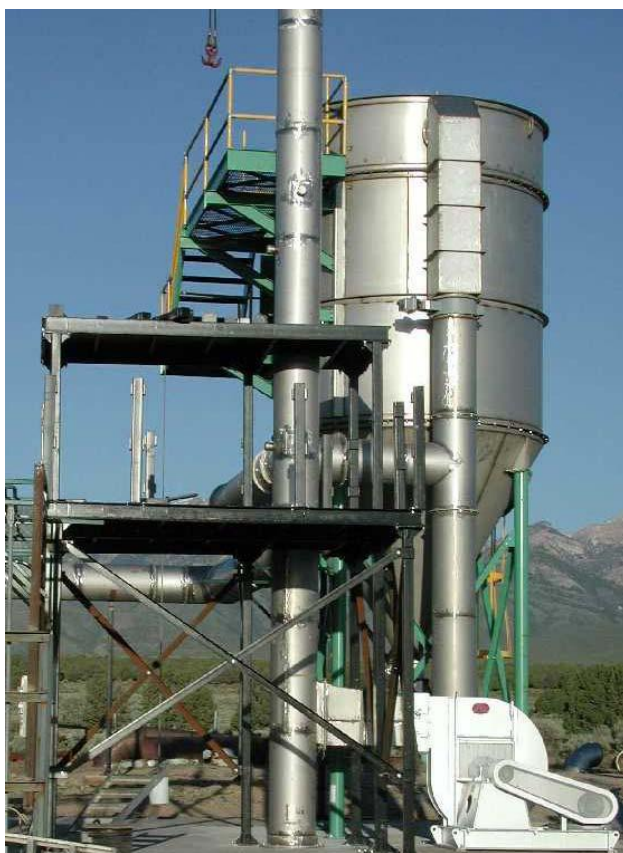


Figure 10. APE 1236M2 furnace stack, TEAD, Tooele, Utah.

3.2.2.1 Sampling Locations

The DF exhausts to a 19.625-in ID stack. Two 3 ¼-in ID ports, located at right angles to each other, are 102 in (5.2 duct-diameters) downstream and 86 in (4.4 duct-diameters) upstream from the nearest flow disturbances (the induced draft fan and in-stack Pitot, respectively). The average stack temperature at the sampling ports during the second field campaign at TEAD was 388.6°F.

3.3 PHYSICAL SET UP AND OPERATION

3.3.1 North Island Aviation Depot

Three sources were tested at the NADEP North Island in San Diego: a chrome plating bath, an electrode-free Ni plating bath, and a smelter/melting pot used to melt the metal alloy Kirksite. The tests were conducted from June 16 to June 20, 2003.

3.3.1.1 Chrome Plating Operation

The chrome plating baths are vented to the roof of the building via ducts that join at a manifold followed by an induction blower. The ABF-LIPS instrument and dual RM 29 sampling trains were set up on the roof of the building. Monitoring ports installed at right angles were already in place for RM sampling in the 49.5-in. diameter duct. A third port was installed prior to testing to accommodate the ABF-LIPS sample probe. All three ports are nearly co-planar, and are located sufficiently downstream of the nearest duct bend to comply with testing requirements to minimize non-laminar flow.

ABF-LIPS required about 1 hr for setup. A laptop computer was used to interface with the ABF-LIPS instrument for control and data storage. The injection points for spiked metals was located in the two stacks from each of the Enforcer III scrubbers at the edge of the roof. Each Enforcer III duct was ported to accept a stainless steel tube, each connected to a nebulizer fed by solutions of heavy metals for spiking. The turbulent flow in this area, prior to elbows and joining of the two ducts, was thought to provide better mixing across the duct diameter than would be obtained in a region of laminar flow.

3.3.1.2 Ni Plating Operation

The NADEP utilizes two electroless Ni tanks located in Building 472. The electroless Ni tanks are part of Line #2, which includes tanks P2-9A, P2-B, P2-10, P2-11, P2-12, and P2-13. Emissions from four of the tanks are collected by 3-inch high slot type hoods on the back side of each tank which are manifolded to one central duct. The front of each tank is equipped with a push air header to provide a slipstream of air to assist in collecting the mist formed during reduction. The emission stream is vented to a demister before entering a 20-hp blower which is manufactured by Barry Blower. The exhaust stack diameter is 28 in.

Tanks P2-11, and P2-13 are 46 in long, 29 in wide, and 36 in deep. The tanks are heated by hot water and have a working volume of 175 gallons.

The sampling location was conducted on the exhaust of the mist eliminator just below roof level inside of the building. Three ports were installed prior to the tests. Equipment for both the RM

and ABF-LIPS were brought to the roof via hydraulic lifts. Metal spiking was performed at the exit of the mist eliminator.

3.3.1.3 Kirksite Furnace

The Kirksite molten alloy furnaces are located inside the shop along the southwest corner of Building 65. The exhaust stacks exit the building near the floor and make a straight vertical run to the roof along the outside of the building. Test ports are installed on the exhaust stack near the roofline of the building. The stack diameter is 34 in. Stack temperature is slightly elevated at a temperature of 105°F. Access to the test ports for the RM sampling was from the roof, and access to the opposing port for ABF-LIPS was achieved using a hydraulic lift. Metals spiking was performed at the suction side of the blower.

3.3.2 Tooele Army Depot

An initial test at TEAD's prototype APE 1236M2 munitions DF in October 2004 was aborted by the end of the first day due to freezing temperatures and blowing snow. A second field test was conducted at TEAD during September 2005. Source testing for multiple metals was conducted in quadruplicate on the inlet to the baghouse by USEPA Method 29. In order to ensure a measureable amount of selected metals in the stack gas, the source was spiked with three different concentrations (low, medium, and high) of Cd, Cr, Ni, Pb, and Hg compounds by using a compressed air aspirator and a peristaltic pump with prepared solutions of Cr, Cd, Ni, Pb, and Hg salts. The furnace was operated without any feed material and the afterburner was turned off. This provided an acceptable test location at the baghouse inlet for comparative testing at relatively constant flow rate and elevated temperature. The metal salts were injected at the afterburner exit about 30 duct diameters upstream of the testing location. The tests were conducted on September 13, 14, and 15, 2005. Professional Environmental Services, Inc. (PES) of Irwindale, California, a participant in the California Air Resources Board's Independent Contractor Program, performed USEPA Method 29 RM stack sampling. West Coast Analytical Service performed analytical work on the samples collected by PES.

The number of traverse points required (six on each of 2 diameters, 90° apart) and their locations are specified in USEPA Method 1. For each test, the ABF-LIPS instrument collected a sample concurrently with the RM for multiple metals.

3.4 SAMPLING/MONITORING PROCEDURES

The experimental design is dictated by PS-10 and Method 301. The primary data quality objective in the field tests was to determine the accuracy of ABF-LIPS relative to the RM, USEPA Method 29. This comparative accuracy is termed RA. Acceptable results for RA per PS-10 are values within $\pm 20\%$ of the RM result. Data quality objectives and measurement parameters applied to these field tests are summarized in Table 3. The full specification for PS-10 is included as Appendix B.

ABF-LIPS was operated concurrently with the RM, USEPA Method 29. The RM probes traversed the stacks/ducts per 40 CFR part 60, Appendix A, Method 1, Sections 2.2 and 2.3. Duct diameters were calculated per 40 CFR part 60, Appendix A, Method 1, Section 2.1. Start and

stop times for both the ABF-LIPS and the RM were coordinated so that results from ABF-LIPS could be averaged to correspond with the time-integrated sample collected by the RM. In effect, each ABF-LIPS sample is an independent analysis, and rather than integrating the ABF-LIPS result, an average is calculated to compare to the RM.

Each test required about 75 to 120 min to complete, depending on the anticipated metal concentrations, with half-hr to one-hr setup/breakdown intervals. Samples from the RM will be delivered to an analytical laboratory and results made available within a month of the test dates. Preliminary results from the ABF-LIPS were available in real time, though post-processing necessary to derive final results was typically not completed until several months after the field work.

3.4.1 NADEP Test

The experimental approach at NADEP was to measure three sources — a chrome plating line, an electroless Ni plating line (both sampled and spiked after emission control devices), and a molten metal (Kirkcaldy) furnace. The sampling procedure at each of the three sources at NADEP differed in terms of the number and duration of RM transverse points as determined by the duct diameter.

A time-integrated filter sample was taken by the USEPA RM for each configuration. ABF-LIPS utilizes an extractive sampling scheme by using the aerosol focusing technology; thus, it was possible for the instrument to perform a six-point or a 12-point sampling configuration similar to the USEPA RM method. Since the ABF-LIPS measurement cycle is shorter than 6 min, it was possible to take multiple measurements for each point before the probe was moved to the next point in corresponding to the RM sampling schedule. Thus, the spatial and temporal variations of the emissions in the source volume (inside the circle) could be resolved, or mapped, while RM could not provide similar information.

Since the measurement resolution in space and time between ABF-LIPS and the RM are so different, it is difficult to compare the continuous measurements of ABF-LIPS with the time-integrated RM result. As a first-order approximation, an unweighted average of all ABF-LIPS measurements was used to compare with the RM results, while the statistics (SD and coefficient of variation) from the ABF-LIPS measurements could be used to understand the variation of source emissions (including spiking consistency). Additional information such as mass flow rate at each probe location could be used as a weight for ABF-LIPS data averaging to more accurately determine the emission rate.

The chrome plating line was sampled using two RMs. Source testing for hexavalent Cr was conducted in triplicate on the common exhaust of both composite mesh pad systems by USEPA Method 306, and source testing for Cd, Cr, and Ni was conducted concurrently by USEPA Method 29. Two methods were chosen to compare RM results for Cr.

Source testing for Cd, Cr, and Ni was conducted in quadruplicate on the exhaust of the mesh pad from the electroless Ni plating line by USEPA Method 29. The first test run was without any spiking and constituted a baseline test for the source.

Source testing for multiple metals (except Hg) was conducted in quadruplicate on the exhaust to atmosphere from the Kirksite furnace by USEPA Method 29. The first test run was not spiked and served as a baseline test for the source.

3.4.1.1 Metals Spiking

Two ultrasonic particle generators were used at NADEP to spike aerosol particles embedded with metals into the exhaust flow upstream of the sampling location. ORNL tested these generators and found that the droplet sizes were about 1.7 micrometers (μm). The droplets were almost immediately dried by the stack flow; the resulting residual size was measured with a particle analyzer to be 1 μm or slightly smaller. This particle size is within the range that allows the ABF-LIPS nozzle to focus. A pre-mixed solution of metal salts was injected into the ducts via the ultrasonic nebulizers. The salts are listed in Table 4.

The concentrations (in units of μg of metal per liter [L] of water) of the target metals, Ni, Cd, and Cr are shown in Table 4. For the spiking solutions, Ni was produced from a reagent-grade NiCl_2 salt, Cd was from CdCl_2 , and Cr was from $\text{K}_2\text{Cr}_2\text{O}_7$ salt. All three salts were reagent-grade. A 500-milliliters (mL) volume was prepared for each of the three solutions which were designated as L for low strength, M for medium, and H for high strength.

Table 4. Solution concentrations of spiked metals (top rows) and run schedule for NADEP listing spiking concentrations (bottom three rows).

Spiking Solution Strengths	Ni	Cr	Cd	Solution Symbol	Units
Low	330	150	153	L	$\mu\text{g/L}$
Mid	702	601	601	M	$\mu\text{g/L}$
High	2727	6000	6003	H	$\mu\text{g/L}$
Date Run Number	1	2	3	4	Location
16-Jun-03	M				Cr site
17-Jun-03	M	H			Cr site
18-Jun-03	Baseline	L	M	H	Ni bath
19-Jun-03	Baseline	L			Kirksite
20-Jun-03	M	H			Kirksite

3.4.1.2 Reference Method Multiple Metals Sampling

The number of traverse points required and their locations (minimum of 8 duct diameters downstream of a flow disturbance and 2 duct diameters upstream to the nearest disturbance) are specified in USEPA Method 1. Prior to source testing, each test location was checked for cyclonic flow by the Pitot tube traverse method. The Pitot tube was rotated through the null point, the angle of which was measured with an incline gage. The source tests on the Ni tanks were conducted on the exhaust of the mist eliminator just below roof level. The source tests on the hard chrome plating tanks were conducted on the common exhaust of both Enforcer III systems prior to the inlet of the blower. The source tests on the Kirksite furnace were conducted on the exhaust to atmosphere at roof level. For each source, the ABF-LIPS instrument collected a

multipoint continuous sample concurrently and in the same plane as the RMs for total Cr and multiple metals.

3.4.1.2.1 Total Cr Reference Method Sampling

Total Cr was measured using USEPA Method 306 (RM). The samples were extracted through a glass nozzle, a Teflon[®] union, a 36 to 60 in glass-lined stainless steel probe, a short length of $\frac{3}{8}$ in Teflon[®] tubing from the probe to the first impinger, two Greenburg-Smith impingers each charged with 100 mL of 0.1 N sodium bicarbonate solution, an empty impinger, an impinger filled with silica gel, a 30-ft umbilical line, a vacuum pump, a dry gas meter, and a calibrated orifice connected to an inclined oil manometer.

The weight of the impinger solution and the weight of the silica gel were recorded before and after each test in order to obtain the moisture content of the stack gas. All sample weights were recorded immediately on sample recovery sheets during charging and sample recovery. Leak checks were performed before and after each test.

The sampling was conducted isokinetically for 120 min at 5 min per point (24 points total), generating a sample size of about 90 cubic ft through the train. Three test runs were made. Field data were recorded on the data sheets shown in Appendix C, which also detail the calculation sheets. Volumetric flow rates of the exhaust duct were calculated from the measured velocity head and the cross-sectional area of the duct. As each traverse point was sampled, the velocity head of the flue gas was measured with an S-type Pitot tube connected to an inclined oil manometer, and the temperature of the flue gas was measured with a chromel-alumel (type K) thermocouple and a digital potentiometer (USEPA Method 2).

The sampling trains were recovered in the PES van on the same day as the sampling. The contents of the impingers were placed in a 500-mL polyethylene container. The sampling train was then rinsed from the third impinger to the nozzle with the charging solution and the rinsate was added to the sample bottle. The impinger solution was chilled to an exit gas temperature of 68°F or less during the tests and kept refrigerated prior to the analyses to prevent degradation of the sample. Disposable vinyl gloves were worn during sample retrieval to prevent contamination.

Laboratory analyses were conducted by West Coast Analytical Service in Santa Fe Springs, California. Total Cr determinations were made by ICP/mass spectrometry (MS). The minimum detection level of the analytical procedure for total Cr, CrT, was 0.2 µg/L. A sample submittal/chain of custody sheet was completed when the samples were submitted. The laboratory analysis report is included in Appendix D.

3.4.1.2.2 Multiple Metals Reference Method Sampling

Multiple metals were measured by using USEPA Method 29. The samples were extracted through a glass nozzle, a Teflon[®] union, a 36 to 60 in glass-lined stainless steel probe, a glass fiber filter in a glass housing, a short length of $\frac{3}{8}$ in Teflon[®] tubing from the probe to the first impinger, two Greenburg-Smith impingers each charged with 100 mL of 5% nitric acid/10% hydrogen peroxide solution, an empty impinger, an impinger filled with silica gel, a 30-ft

umbilical line, a vacuum pump, a dry gas meter, and a calibrated orifice connected to an inclined oil manometer. The moisture content was less than 2% so the probe and filter were unheated.

The weight of the impinger solution and the weight of the silica gel were recorded before and after each test to obtain the moisture content of the stack gas. All sample weights were recorded immediately on sample recovery sheets during charging and sample recovery. Leak checks were performed before and after each test.

The sampling was conducted isokinetically for 72 to 120 min at 3 to 5 min per point (24 points total), generating a sample size of about 54 to 90 cubic ft through the train. Three to four test runs were made. Field data were recorded on the data sheets shown in Appendix C, which also include the calculation sheets. Volumetric flow rates of the exhaust duct were calculated from the measured velocity head and the cross-sectional area of the duct. As each traverse point was sampled, the velocity head of the flue gas was measured with an S-type Pitot tube connected to an inclined oil manometer, and the temperature of the flue gas was measured with a chromel-alumel (type K) thermocouple and a digital potentiometer (USEPA Method 2).

The sampling trains were recovered on the same day as the sampling. The contents of the impingers were placed in a 500-mL polyethylene container. The sampling train was then rinsed with 0.1 N nitric acid solution. The rinse from the third impinger to the back of the filter bell was added to the sample bottle, and the rinse from the nozzle to the front of the filter bell was placed in a 250-mL sample bottle. The impinger solution was chilled to an exit gas temperature of 68°F or less during the tests and kept refrigerated prior to the analyses to prevent degradation of the sample. Disposable vinyl gloves were worn during sample retrieval to prevent contamination.

Laboratory analyses were conducted by West Coast Analytical Service in Santa Fe Springs, California. Multiple metals determinations (except Hg) were made by ICP/MS. A sample submittal/chain of custody sheet was completed when the samples were submitted. The laboratory analysis report is included in Appendix D.

3.4.2 Tooele Army Depot Testing

The tests at TEAD were performed using the prototype munitions DF, APE 1236M2, with no feed (since Pb in ammunition could overwhelm the levels of other metals). The furnace and induction fan were switched on to normal operational mode, but the afterburner was off since the injection point for the spiked metals was located just downstream from the afterburner. This resulted in a distance of about 30 duct diameters between the metals spiking location and the RM sampling point.

3.4.2.1 Metals Spiking

The stack was spiked with an aerosol of heavy metals pumped from a reservoir containing dissolved heavy metals. Plastic vials containing pre-weighed amounts of metals salts corresponding to low, medium, and high concentrations were dissolved into an appropriate volume of deionized (DI) water in 32-gallon plastic tubs. DI water was produced on site using an industrial three-tank resin deionizing system (anion, cation, and mixed bed tanks). The nebulizer system consisted of a high pressure pump feeding a fogging nozzle inserted into the furnace

exhaust via a small hole in the duct approximately 10 ft downstream of the afterburner. Figure 11 shows the platform used to support the spiking equipment.



Figure 11. Metals spiking platform at TEAD APE 1232M2 prototype deactivation furnace during September 2005 test.
(afterburner is at left)

Spiking began after steady-state conditions were met, i.e., when temperature and flow had stabilized. A stable temperature and flow measurement ensured that the system had reached a steady state, but did not necessarily ensure that the particle concentration had also reached a steady state. Thus, a suite of aerosol size-measurement devices was used, including a scanning mobility particle sizer, which measures particles of diameter from 6 nm to 700 nm, and an aerodynamic particle sizer, which measures particles of diameter from 500 nm to 20 μm . These two instruments scanned for particle size distribution continuously. Once the distributions were within a $\pm 20\%$ target range, the system was considered to have reached a steady-state condition and the ABF-LIPS and RM sampling commenced.

The test was run in quadruplicate at each of three spiking concentrations: low, medium, and high. Five metals were spiked: Cd, Cr, Pb, Ni, and Hg. Target concentrations for the spike metals in the stack are shown in Table 5. These concentration levels were selected based on those used in previous CEMS tests (Haas et al., 1997; Dunn et al., 1998) in industrial waste incinerator emissions. These concentrations are also in the detectable range for both measurement methods so that comparable results in a linear range would be obtained.

Table 5. Target concentrations for spiked metals in flue gas at TEAD.

Element	Low $\mu\text{g}/\text{m}^3$	Medium $\mu\text{g}/\text{m}^3$	High $\mu\text{g}/\text{m}^3$
Cd	70	100	500
Cr	5	50	200
Hg	100	500	1000
Ni	200	500	1000
Pb	10	25	50

ABF-LIPS was set up on the high platform of the exhaust stack, and the RM equipment was located on the lower platform, approximately 10 ft upstream of the ABF-LIPS sampling location. The ABF-LIPS instrumentation was lifted to the upper platform using a forklift. Each platform level accesses two ports 90° apart. Photos of the instrumentation are included as Figures 12 through 15.



Figure 12. Sampling location for ABF-LIPS and reference method during September 2005 test on platform prior to baghouse.
(platform is center left accessing horizontal duct)



Figure 13. Sampling at TEAD, September 2005 test.
(ABF-LIPS is to the right side of platform, and the reference method is to the left side of the platform.)



Figure 14. ABF-LIPS instrument (cube structure at left) and laptop used for control and data storage at TEAD during September 2005 test.



Figure 15. Reference method sampling apparatus (Method 29) at TEAD September 2005 test.

ABF-LIPS baseline measurements (zero) were made at the beginning and end of the test day and at the start of each test run using ambient air.

ABF-LIPS instrument drift was determined by inspecting the spectral peaks of the first and fourth consecutive run of a given spike concentration.

3.4.2.2 Reference Method Multiple Metals Sampling

Multiple metals were measured at TEAD using RM USEPA Method 29. Samples were extracted through a glass nozzle, a Teflon[®] union, a 36 in glass-lined stainless steel probe, a quartz filter in a glass housing, a set of Greenburg-Smith impingers, a 30-ft umbilical line, a vacuum pump, a dry gas meter, and a calibrated orifice connected to an inclined oil manometer. The moisture content was less than 3% so the probe was unheated and the filter was heated to 250°F. In the impinger set, the first two impingers were each charged with 100 mL of 5% nitric acid/10% hydrogen peroxide solution, the third impinger was empty, the fourth and fifth impingers were each charged with 100 mL of 4% potassium permanganate/10% sulfuric acid solution, and the sixth impinger was filled with silica gel.

The weight of the impinger solutions and the weight of the silica gel were recorded before and after each test to obtain the moisture content of the stack gas. All sample weights were recorded immediately on sample recovery sheets during charging and sample recovery. Leak checks were performed before and after each test.

The sampling was conducted isokinetically for 84 min at 7 min per point (12 points total), generating a sample size of about 75 cubic ft through the train. Twelve test runs were made: four

at each of three spiking levels. Field data were recorded on the data sheets shown in Appendix C, which also includes the calculation sheets. Volumetric flow rates of the exhaust duct were calculated from the measured velocity head and the cross-sectional area of the duct. As each traverse point was sampled, the velocity head of the flue gas was measured with an S-type Pitot tube connected to an inclined oil manometer, and the temperature of the flue gas was measured with a chromel-alumel (type K) thermocouple and a digital potentiometer (USEPA Method 2).

The sampling trains were recovered on the same day as the sampling. The contents of the first three impingers were placed in a 500-mL polyethylene container. The sampling train was then rinsed with 0.1 N nitric acid solution. The rinse from the third impinger to the back of the filter bell was added to the sample bottle, and the rinse from the nozzle to the front of the filter bell was placed in a 250-mL polyethylene sample bottle. The contents of the third and fourth impingers were placed in a 500-mL precleaned amber glass bottle. The same impingers were then rinsed three times with distilled water and the rinse was added to the glass bottle. The same two impingers were then rinsed with 25 mL of 8 N hydrochloric acid and the rinse was placed in a 250-mL amber glass bottle along with 200 mL of distilled water. Individual volumes for the rinses were obtained by recording the bottle weights before and after adding the rinses.

The impinger solution was chilled to an exit gas temperature of 68°F or less during the tests and kept refrigerated prior to the analyses to prevent degradation of the sample. Disposable vinyl gloves were worn during sample retrieval to prevent contamination.

Laboratory analyses were conducted by West Coast Analytical Service in Santa Fe Springs, California. Multiple metals determinations for Cr, Cd, Pb, and Ni were made by ICP/MS. Hg determinations were made by cold vapor/atomic fluorescence spectrometry. A sample submittal/chain of custody sheet was completed when the samples were submitted. The laboratory analysis report is included in Appendix D.

Calculations were made from the field data sheets to determine sample volume, molecular weight, velocities, flow rate, isokinetic variation, and component concentrations for the tests.

3.5 ANALYTICAL PROCEDURES

USEPA Method 301, as specified by USEPA, is to be used whenever a source owner or operator proposes a test method to meet USEPA requirements in the absence of a validated method. This method includes procedures for determining and documenting the quality, i.e., systematic error (bias) and random error (precision), of the measured concentrations from an effected source. This method is applicable to various waste media and will be used to verify the performance of the ABF-LIPS, for which there is no standard USEPA method. USEPA Performance PS-10 is a specific guidance to Method 301, which describes performance criteria for multi-metals CEMS.

A multi-metals CEMS must be capable of measuring the total concentrations of two or more of the following metals in both their vapor and solid states: Sb, As, Ba, Be, Cd, Cr, Pb, Hg, Ag, Tl, Mn, Co, Ni, and Se. The method compares a standard RM (USEPA Method 29) with the instrument to be validated. A minimum of nine pairs of data are collected on two or more metals, and the method undergoing validation must be accurate to within $\pm 20\%$ of the RM. PS-10 is included as Appendix B.

USEPA Method 29 is applicable for the determination of metals emissions from stationary sources and may be used to determine particulate emissions in addition to the metals emissions if the prescribed procedures and precautions are followed. USEPA Method 29 is the industry standard as the most appropriate means of multi-metal analyses for source emissions. The method draws stack emissions through a filter and a series of impingers, providing a 1- to 3-hr average concentration. The filters and impinging solutions are delivered to an analytical laboratory for metals analysis.

Other analytical procedures have been previously described in Section 3.4.

4.0 PERFORMANCE ASSESSMENT

4.1 PERFORMANCE DATA

4.1.1 NADEP

Three sources were tested at NADEP: a Cr plating bath exhaust, an electroless Ni plating bath exhaust, and a Kirksite furnace exhaust. Sampling locations were located after emission control devices on the Cr and Ni plating exhausts. All sources were spiked with three concentrations of an aerosol of metals containing Cd, Cr, and Ni.

Calculations were made from the field data sheets to determine sample volume, molecular weight, velocities, flow rate, isokinetic variation, and component concentrations for the tests. An interim report for the NADEP results is included as Appendix D.

4.1.1.1 Cr Plating Reference Method Source Test

Table 6 summarizes the results of the Cr testing by USEPA Method 306 on the Enforcer III exhaust. The spiking levels for the three test runs were: none, medium, and high, respectively (the low Cr run was aborted due to failure of the spiking method at an unknown point in the run). The total Cr concentrations for the three USEPA 306 test runs were 0.00017, 0.00012, and 0.00096 mg/DSCM, respectively. Cumulative run times of sample collection were 120 min; start and stop times span greater periods because some time is required for probe repositioning during transect shifts. Results are shown graphically in Figure 16 (with results from Method 29 described in the following paragraph). The total Cr emission rates for the three USEPA 306 test runs were 9.5, 6.6, and 53.2 mg/hr, respectively.

**Table 6. Reference method results by USEPA Method 306 for
Cr plating exhaust, NADEP 2003.**

Test Number:	1	2	3
Sampling Date:	6/16/03	6/17/03	6/17/03
Sample Number:	472-1	472-3	472-5
Spiking:	None	Medium	High
<u>Flue Gas</u>			
Temperature, °F	71	72	73
Velocity, ft/sec	42.4	42.5	42.5
Static pressure, in of H ₂ O	-9.5	-9.5	-9.5
Stack dimension, in	50	50	50
Stack area, ft ²	13.6	13.6	13.6
Flow rate, ACFM ¹	34,600	34,700	34,700
Flow rate, DSCFM ²	32,800	32,900	32,700
Moisture, % v/v	1.8	1.8	2.1

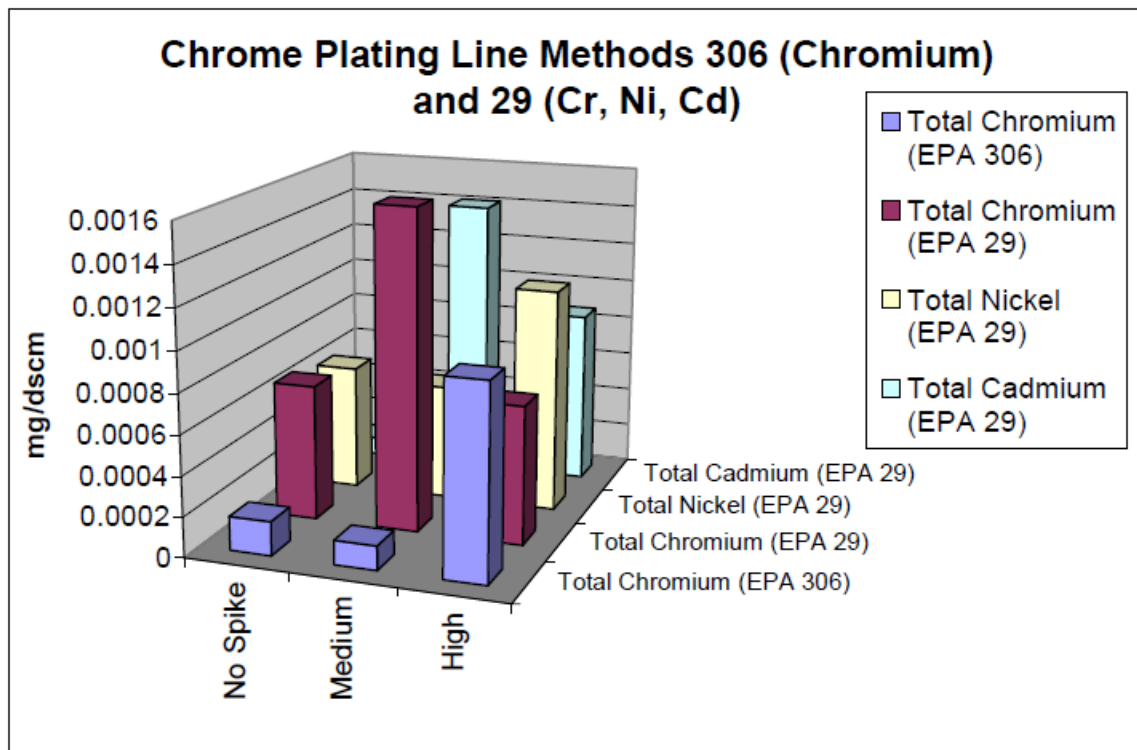
**Table 6. Reference method results by USEPA Method 306 for
Cr plating exhaust, NADEP 2003. (continued)**

Test Number:	1	2	3
Sampling Date:	6/16/03	6/17/03	6/17/03
Sample Number:	472-1	472-3	472-5
<u>Metals</u>			
Sample start	16:48	09:57	13:56
Sample stop	18:54	12:03	16:01
Sampling time, min	120	120	120
Sample volume, DSCF ³	82.66	82.21	81.40
Isokinetic rate, %	101.7	100.9	100.5
Concentration, mg/DSCM	0.00017	0.00012	0.00096
Emission rate, mg/hr	9.5	6.6	53.2

¹ACFM = actual cubic feet per minute

²DSCFM = dry standard cubic feet per minute

³DSCF = dry standard cubic feet



**Figure 16. Comparison of results of reference method testing using
two different methods (USEPA Methods 306 and 29) simultaneously for Cr showing
disparity of results (two front-most rows).
(Ni and Cd results from Method 29 are also shown.
Chrome plating bath exhaust at NADEP, 2003.)**

Table 7 summarizes the results of the metals testing by USEPA Method 29 made on the Enforcer III exhaust concurrently with the USEPA Method 306 sampling. The total Cr concentrations for the three USEPA 29 test runs were 0.00068, 0.00116, and 0.00069 mg/DSCM, respectively. Results are shown graphically in Figure 16. The total Cr emission rates for the three USEPA 29 test runs were 39.3, 66.6, and 39.8 mg/hr, respectively. The total Ni concentrations for the three USEPA 29 test runs were 0.00063, 0.00058, and 0.00112 mg/DSCM, respectively. The total Ni emission rates for the three USEPA 29 test runs were 36.5, 33.2, and 64.5 mg/hr, respectively. The total Cd concentrations for the three USEPA 29 test runs were 0.00009, 0.00141, and 0.00087 mg/DSCM, respectively. The total Cd emission rates for the three USEPA 29 test runs were 5.2, 80.9, and 50.0 mg/hr, respectively. Except for the Cd on the second and third runs, the blank corrections for all three test runs were greater than 20% of the total collected in the sample. A high ratio of blank to sample mass for any given metal makes the accuracy of the data questionable because the amount of metal collected is too close to the background level of that metal in the sampling train.

**Table 7. Reference method results by USEPA Method 29 for
Cr plating exhaust, NADEP 2003.**

Test Number:	1	2	3
Sampling Date:	6/16/03	6/17/03	6/17/03
Sample Number:	472-2	472-4	472-6
Spiking:	None	Medium	High
Flue Gas			
Temperature, °F	69	72	72
Velocity, ft/sec	43.5	43.4	43.9
Static pressure, in of H ₂ O	-9.5	-9.5	-9.5
Stack dimension, in	50	50	50
Stack area, ft ²	13.6	13.6	13.6
Flow rate, ACFM ¹	35,500	35,400	35,800
Flow rate, DSCFM ²	33,900	33,700	34,000
Moisture, % v/v	1.6	1.7	1.7
Metals			
Sample start	16:49	09:58	13:56
Sample stop	18:55	12:05	16:02
Sampling time, min	120	120	120
Sample volume, DSCF ³	110.2	108.0	110.2
Isokinetic rate, %	100.7	99.4	100.5
Concentration, mg/DSCM			
Total Cr	*0.00068	*0.00116	*0.00069
Total Ni	*0.00063	*0.00058	*0.00112
Total Cd	*0.000090	0.00141	0.00087
Emission rate, mg/hr			
Total Cr	*39.3	*66.6	*39.8
Total Ni	*36.5	*33.2	*64.5
Total Cd	*5.2	80.9	50.0

*Blank correction greater than 20% of total collected in sample.

¹ACFM = actual cubic feet per minute

²DSCFM = dry standard cubic feet per minute

³DSCF = dry standard cubic feet

4.1.1.2 Ni Plating Bath Exhaust Reference Method Source Test

Table 8 summarizes the results of the metals testing by USEPA Method 29 made on the Ni tank mist eliminator exhaust. The spiking levels for the four test runs were: none, low, medium, and high, respectively. The total Cr concentrations for the four USEPA 29 test runs were 0.00025, 0.00504, 0.00397, and 0.00653 mg/DSCM, respectively. The total Cr emission rates for the four USEPA 29 test runs were 16.3, 32.4, 25.8, and 42.2 mg/hr, respectively. Results are shown graphically in Figure 17. The total Ni concentrations for the four USEPA 29 test runs were 0.00402, 0.00291, 0.00291, and 0.00309 mg/DSCM, respectively. The total Ni emission rates for the four USEPA 29 test runs were 26.0, 18.8, 18.9, and 20.0 mg/hr, respectively. The total Cd concentrations for the four USEPA 29 test runs were 0.00045, 0.00059, 0.00125, and 0.00194 mg/DSCM, respectively. The total Cd emission rates for the four USEPA 29 test runs were 2.9, 3.8, 8.1, and 12.6 mg/hr, respectively. On all of the Cr runs and the second Cd run, the blank corrections were greater than 20% of the total collected in the sample. A high ratio of blank to sample mass for any given metal makes the accuracy of the data questionable because the amount of metal collected is too close to the background level of that metal in the sampling train.

Table 8. Reference method results for Ni plating exhaust, NADEP 2003.

Test Number:	1	2	3	4
Sampling Date:	6/18/03	6/18/03	6/18/03	6/18/03
Sample Number:	472-7	472-8	472-9	472-10
Spiking:	None	Low	Medium	High
<u>Flue Gas</u>				
Temperature, °F	78	78	78	79
Velocity, ft/sec	21.2	21.1	21.3	21.3
Static pressure, in of H ₂ O	-0.65	-0.65	-0.65	-0.65
Stack dimension, in	24	24	24	24
Stack area, ft ²	3.14	3.14	3.14	3.14
Flow rate, ACFM ¹	3990	3970	4010	4010
Flow rate, DSCFM ²	3800	3790	3820	3800
Moisture, % v/v	2.3	2.1	2.3	2.5
<u>Metals</u>				
Sample start	09:45	13:07	15:05	16:58
Sample stop	11:50	14:23	16:21	18:14
Sampling time, min	120	72	72	72
Sample volume, DSCF ³	77.08	45.66	46.97	45.34
Isokinetic rate, %	100.1	99.0	101.1	98.0
<u>Concentration, mg/DSCM</u>				
Total Cr	*0.00025	*0.00504	*0.00397	*0.00653
Total Ni	0.00402	0.00291	0.00291	0.00309
Total Cd	0.00045	*0.00059	0.00125	0.00194
<u>Emission rate, mg/hr</u>				
Total Cr	*16.3	*32.4	*25.8	*42.2
Total Ni	26.0	18.8	18.9	20.0
Total Cd	2.91	*3.81	8.11	12.6

*Blank correction greater than 20% of total collected in sample.

¹ACFM = actual cubic feet per minute

²DSCFM = dry standard cubic feet per minute

³DSCF = dry standard cubic feet

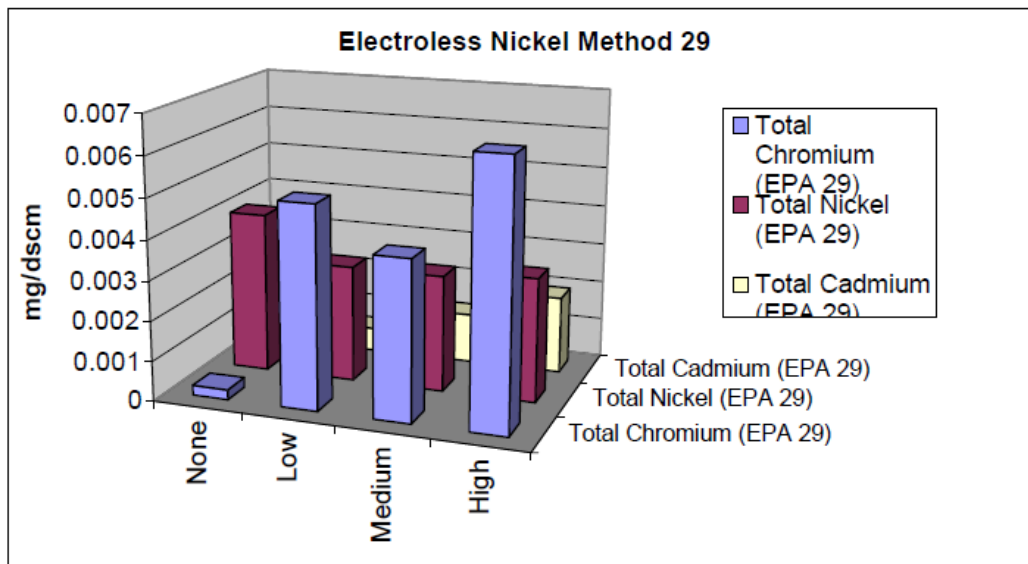


Figure 17. Electroless Ni plating bath exhaust stack Method 29 results during baseline (no spiking - none), and after spiking three concentrations of metals (low, medium, high).

4.1.1.3 KirkSITE Furnace Exhaust Reference Method Source Test

Table 9 summarizes the results of the metals testing by USEPA Method 29 made on the KirkSITE furnace exhaust. The spiking levels for the four test runs were: none, low, medium, and high, respectively. Except for the Sb on the first and third runs, the blank corrections for all four test runs were greater than 20% of the total collected in the sample. A high ratio of blank to sample mass for any given metal makes the accuracy of the data questionable because the amount of metal collected is too close to the background level of that metal in the sampling train. Results are shown graphically in Figure 18.

Table 9. Reference method results for KirkSITE furnace exhaust, NADEP 2003.

Test Number:	1	2	3	4
Sampling Date:	6/19/03	6/19/03	6/20/03	6/20/03
Sample Number:	65-1	65-2	65-3	65-4
Spiking:	None	Low	Medium	High
<u>Flue Gas</u>				
Temperature, °F	81	80	77	76
Velocity, ft/sec	43.5	43.6	42.9	43.5
Static pressure, in of H ₂ O	0.15	0.15	0.10	0.12
Stack dimension, in	34	34	34	34
Stack area, ft ²	6.30	6.30	6.30	6.30
Flow rate, ACFM ¹	16,500	16,500	16,200	16,400
Flow rate, DSCFM ²	15,600	15,600	15,600	15,800
Moisture, % v/v	2.0	2.3	2.1	2.1
<u>Metals</u>				
Sample start	11:36	14:58	09:13	11:08
Sample stop	13:38	16:12	10:28	12:23
Sampling time, min	120	72	72	72

Table 9. Reference method results for Kirksite furnace exhaust, NADEP 2003 (continued).

Test Number:	1	2	3	4
Sampling Date:	6/19/03	6/19/03	6/20/03	6/20/03
Sample Number:	65-1	65-2	65-3	65-4
Sample volume, DSCF ³	83.90	50.42	49.65	50.05
Isokinetic rate, %	100.3	100.4	99.4	98.9
Concentration, mg/DSCM				
Total Cr	*0.00151	*0.00262	*0.00449	*0.00623
Total Ni	*0.00052	*0.00099	*0.00105	*0.00118
Total Cd	*0.00013	*0.00020	*0.00018	*0.00044
Total Sb	0.00037	*0.00013	0.00144	*0.00010
Total Be	*0.00022	*0.00020	*0.00034	*0.00067
Total Cu	*0.00160	*0.00125	*0.00358	*0.00214
Total Pb	*0.00797	*0.00689	*0.00472	*0.00482
Total Mn	*0.00006	*0.00043	*0.00037	*0.00100
Emission rate, mg/hr				
Total Cr	*40.1	*69.7	*119	*167
Total Ni	*13.9	*26.2	*27.7	*31.7
Total Cd	*3.68	*5.20	*4.62	*11.7
Total Sb	9.83	*3.51	38.0	*2.70
Total Be	*5.92	*5.20	*8.94	*17.9
Total Cu	*42.4	*33.2	*94.5	*57.3
Total Pb	*212	*183	*125	*129
Total Mn	*1.54	*11.3	*9.76	*26.9

*Blank correction greater than 20% of total collected in sample.

Note: Ba and Zn could not be determined due to high filter background.

¹ACFM = actual cubic feet per minute

²DSCFM = dry standard cubic feet per minute

³DSCF = dry standard cubic feet

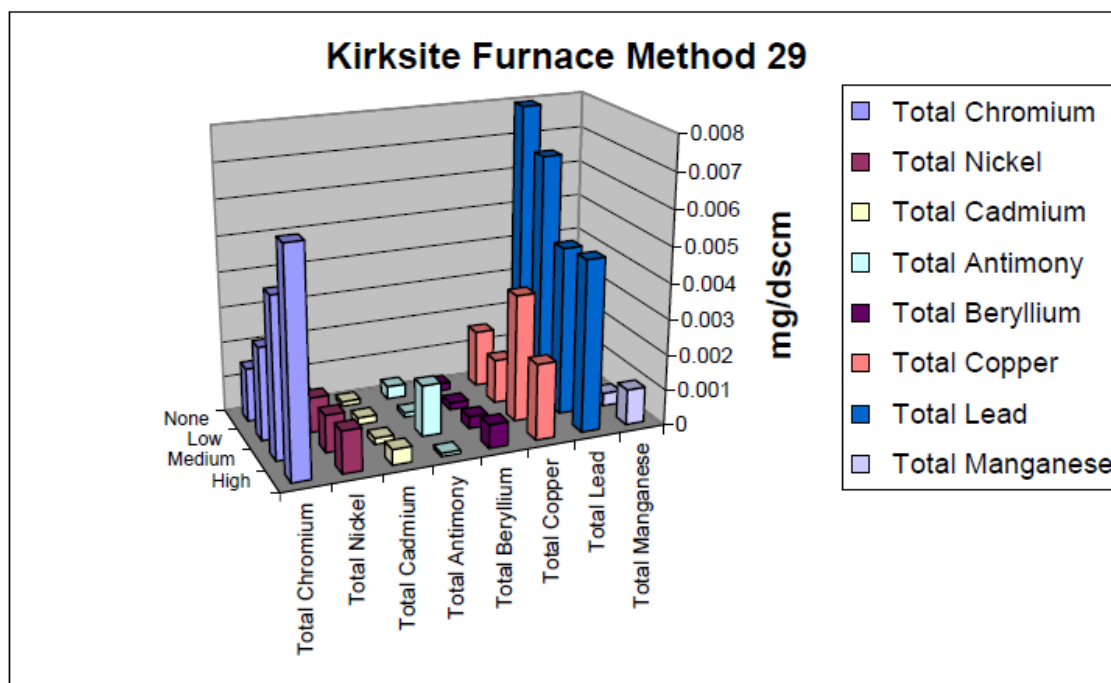


Figure 18. Reference method results for Kirksite Furnace at NADEP.

4.1.1.4 ABF-LIPS Cr Plating Bath and Ni Plating Bath Exhausts

ABF-LIPS measurements at the Cr plating line exhaust and at the electroless Ni exhaust did not yield quantifiable characteristic emission line spectra for the elements of interest (Cr, Cd, and Ni). Signal-to-noise ratios were too low to enable a positive identification of the three elements; spectra may have been collected with an incorrect exposure time setting. Table 10 presents the RM results for the Cr plating exhaust; note that Cr was measured using two USEPA Methods, Methods 29 and 306. Agreement between these two standard methods was generally poor (beyond the 20% RA requirement for new methods per PS-10), suggesting that the RMs, particularly at low concentrations, have significant error. (The low concentration spike run was aborted when it was found the spike delivery system had failed at an unknown point during the run.) Table 11 presents the RM results for the electroless Ni exhaust.

Table 10. Comparison of results for two different reference methods for Cr at Cr plating bath exhaust stack, NADEP.

Chrome Plating Line (sampled after Enforcer III)			
Reference Method Results (mg/DSCM)	No Spike	Medium	High
Total Cr (USEPA Method 306)	0.00017	0.00012	0.00096
Total Cr (USEPA Method 29)	0.00068	0.0016	0.00069
Total Ni (USEPA Method 29)	0.00063	0.00058	0.00112
Total Cd (USEPA Method 29)	0.00009	0.00141	0.00087

(Ni and Cd result also shown using Method 29)

Table 11. Reference method results at electroless Ni plating bath exhaust stack, NADEP.

Electroless Ni (sampled after mist pad)				
	None	Low	Medium	High
Total Cr (USEPA Method 29)	0.00025	0.00504	0.00397	0.00653
Total Ni (USEPA Method 29)	0.00402	0.00291	0.00291	0.00309
Total Cd (USEPA Method 29)	0.00045	0.00059	0.00125	0.00194

The last source tested at NADEP was the Kirksite furnace. ABF-LIPS exposure times were adjusted prior to these tests, which resulted in quantifiable emission spectra. These data are summarized in Table 12, together with SDs (SDs were calculated based on six data points corresponding to six probe positions in the duct stack). Only one run at each concentration was performed, so the RM does not have calculable SD. Data are presented graphically in Figures 19 through 21.

Table 12. Cr plating bath exhaust measurements using ABF-LIPS and reference method.

Element	Measurement Method	No Spike	Low Spike	Std. Dev Low	Medium Spike	Std. Dev Med.	High Spike	Std. Dev. h
Cr	USEPA reference method	0.00151	0.00262		0.00449		0.00623	
Cr	ABF-LIPS		54,068	32,813	86,766	19,187	1828	2085
Ni	USEPA reference method	0.00052	0.00099		0.00105		0.00118	
Ni	ABF-LIPS		12,391	9174	11,109	3642	1868	1175
Cd	USEPA reference method	0.00013	0.0002		0.00018		0.00044	
Cd	ABF-LIPS		8235	7503	8794	2032	6940	2765

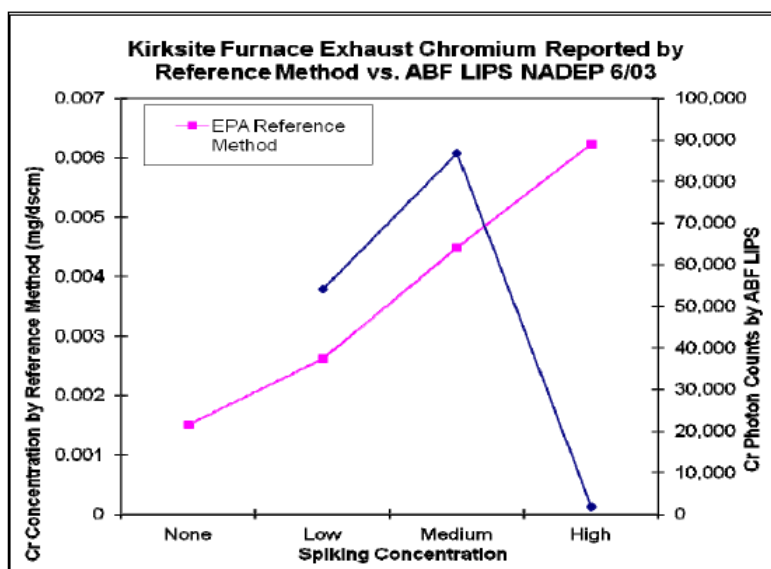


Figure 19. ABF-LIPS results versus reference method for Cr at Kirksite Furnace, NADEP.

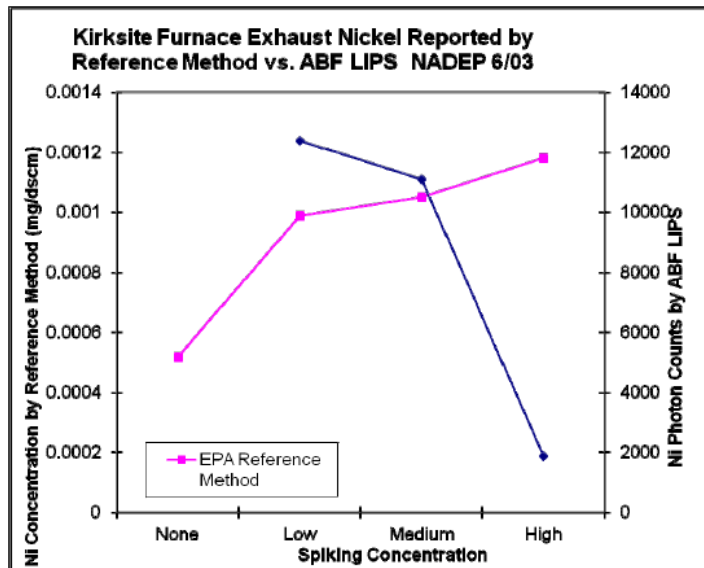


Figure 20. ABF-LIPS results versus reference method for Ni at Kirksite Furnace, NADEP.

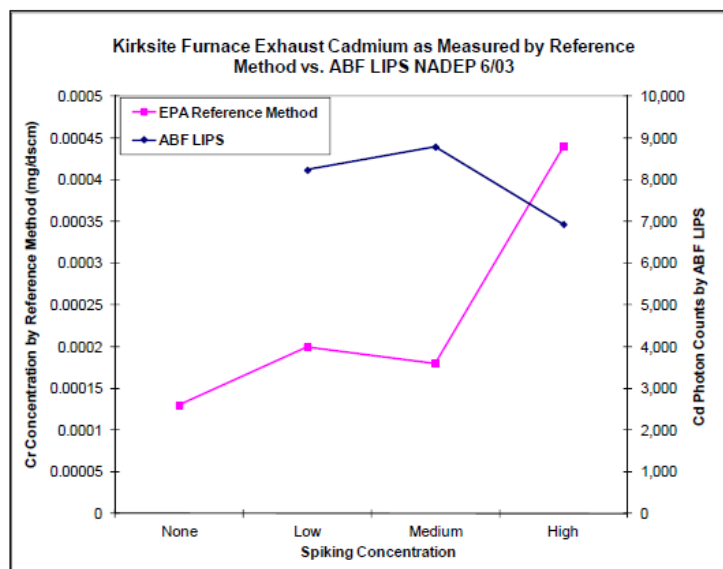


Figure 21. ABF-LIPS results versus reference method for Cd at Kirksite Furnace, NADEP.

4.1.2 TEAD

4.1.2.1 October 2004 Test

The first field test at TEAD in October 2004 was aborted during the first day due to failure of ABF-LIPS equipment associated with unexpectedly cold and snowy conditions. Three test runs were completed, but only one of the RM results was analyzed to determine whether spiked metals could be detected. It was noted that metals were precipitating in the stock feed solution due to the cold weather. A heating bath (a crock pot) was obtained to prevent precipitation, but this was only partly successful (some of the precipitate disappeared, but not all). Together with the equipment malfunction of ABF-LIPS (condensation was forming on the detector, though this

was partly remedied with a blow dryer), the test was aborted. The low concentration spike RM is summarized in Table 13. Complete data from that run are included in Appendix C.

Table 13. Reference method result for low concentration spike run from October 2004 test at TEAD prior to canceling field test.

Element	Concentration	Units
[Ni] =	0.044440	mg/DSCM (m(Ni)6/Vmstd)
[Cd] =	0.022926493	mg/DSCM (m(Cd)6/Vmstd)
[Cr] =	0.009092186	mg/DSCM (m(Cr)6/Vmstd)
[Pb] =	0.003225116	mg/DSCM (m(Pb)6/Vmstd)
[Hg] =	0.032193138	mg/DSCM (m(Hg)8/Vmstd)

(mg/DSCM = milligrams per dry standard cubic meter)

4.1.2.2 September 2005 Test

The second field test at TEAD was carried out September 13-15, 2005. Weather conditions were favorable (mostly sunny, 55 to 75°F); freezing of standard solutions was not an issue, and the condensation issue on the instrument was remedied by incorporating an air dryer (desiccant). An improved metals spiking system had been developed consisting of a high pressure pump feeding a fogging nozzle (previously an ultrasonic nebulizer had been used but proved unreliable). Five metals were spiked (Cr, Cd, Ni, Pb, Hg). Quadruplicate runs at each of three spiking concentrations (low, medium, high) were carried out, for a total of 12 runs. Results are summarized in Table 14. The results include the average of the quadruplicate runs for both the RM and ABF-LIPS, together with their SD. Figures 22 through 26 present the data graphically.

Table 14. Results of September 2005 field test at TEQAD comparing ABF-LIPS and reference method.

Element	Measurement Method	Low Spike	Std. Dev.	Medium Spike	Std. Dev.	High Spike	Std. Dev.
Cr	USEPA reference method	5.7	2.6	2.8	1.5	148.4	12.0
Cr	ABF-LIPS	0.0	3.0	294.0	58.8	1279.0	383.7
Ni	USEPA reference method	27.0	7.6	19.0	19.7	604.0	54.3
Ni	ABF-LIPS	11.0	3.5	1189.0	345.0	1458.0	452.0
Cd	USEPA reference method	61.1	39.1	30.6	8.1	141.3	26.2
Cd	ABF-LIPS	0.0	35.1	252.0	73.1	282.6	98.9
Pb	USEPA reference method	375.3	104.5	204.1	67.4	224.6	44.9
Pb	ABF-LIPS	33.0	39.4	245.0	119.5	868.0	118.4
Hg	USEPA reference method	184.8	38.0	189.4	105.9	363.2	600.3
Hg	ABF-LIPS	194.0	205.6	537.0	145.0	1016.0	274.3

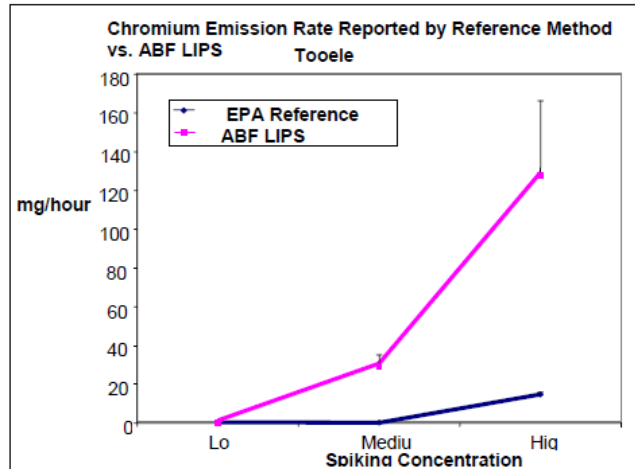


Figure 22. Cr emission rates, with error bars representing one SD (only positive half shown) as measured by ABF-LIPS and the reference method at TEAD

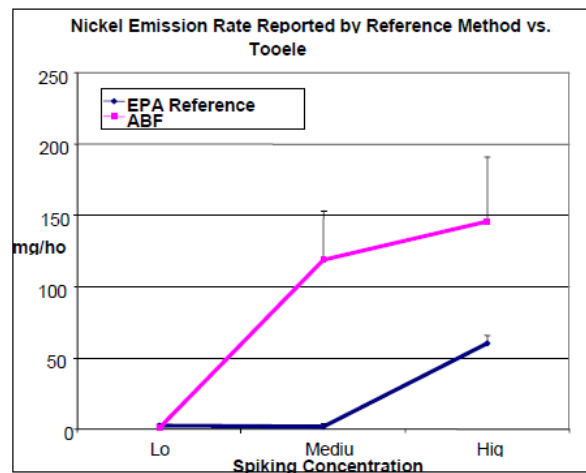


Figure 23. Ni emission rates, with error bars representing one SD (only positive half shown) as measured by ABF-LIPS and the reference method at TEAD.

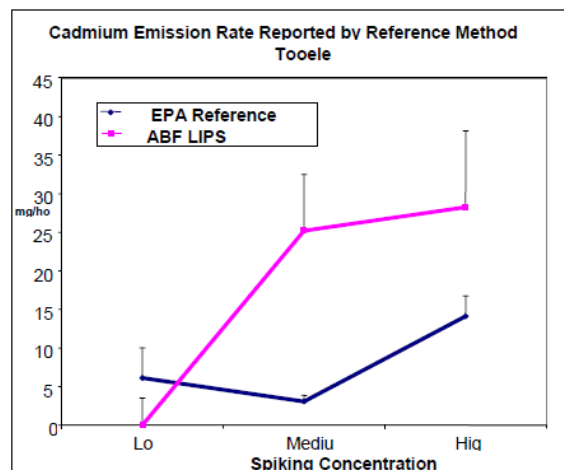


Figure 24. Cd emission rates, with error bars representing one SD (only positive half shown) as measured by ABF-LIPS and the reference method at TEAD.

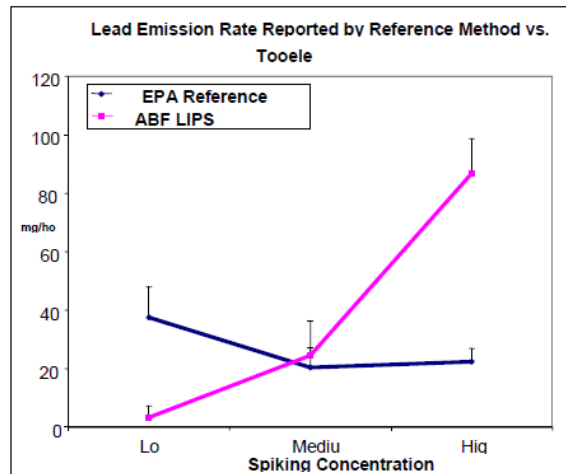


Figure 25. Pb emission rates, with error bars representing one SD (only positive half shown) as measured by ABF-LIPS and the reference method at TEAD

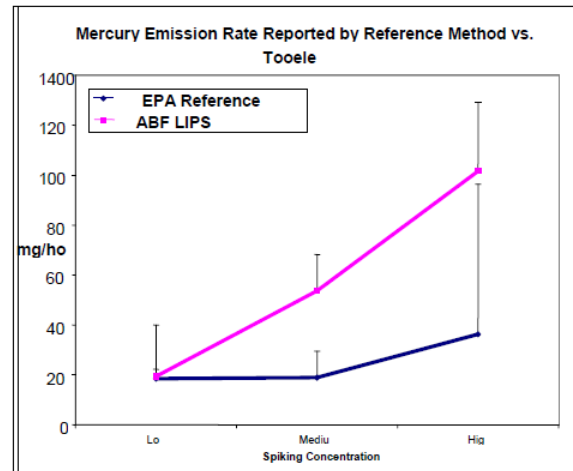


Figure 26. Hg emission rates, with error bars representing one SD (only positive half shown) as measured by ABF-LIPS and the reference method at TEAD

4.2 PERFORMANCE CRITERIA

PS-10 provides specification and test procedures for CEMS in stationary sources. It includes installation and measurement location specifications, performance specifications, test procedures, and data reduction procedures. Specifications from PS-10 pertinent to the validation testing of ABF-LIPS include:

- **RA.** The RA of the CEMS must be no greater than 20% of the mean value of the RM test data in terms of units of the emission standard for each metal, or 10% of the applicable standard, whichever is greater.

This objective was assessed by comparing the RM results (time-averaged concentration) with that of the test instrument results (after data processing and averaging of multiple measurements).

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

CD was assessed by comparing the output (photon counts) of the test instrument using the middle concentration spiking solution at the beginning of each test day (calibration) with the output at the end of the test day (or at the end of the runs for that source, whichever came first) using the same spiking solution.

- **Zero Drift.** The CEMS design must allow the determination of CD 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% of the emission limit value). The CEMS zero point for each metal shall not drift by more than 5% of the emission standard for that metal.

Zero drift was measured by performing the daily zero air calibration (the test instrument measured “zero air” to verify that there were zero photon counts) and comparing this result to the result at the end of the day or end of the test source runs.

- **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.

Sampling and response time is nearly instantaneous and was not formally measured. The number of readings used to determine an average value is variable, and this can be thought of as a sampling/response time though the variation associated with such measurements are a function of the variability in the source stream rather than instrument/measurement variability.

- **Response Time for Instantaneous, Continuous CEMS.** The response time for the CEMS must not exceed 2 min to achieve 95% of the final stable value.

As stated earlier, the response time for ABF-LIPS is nearly instantaneous and was thus not measured during field tests.

- **Capability in Various Environments and Conditions.** The instrument was tested in climates ranging from freezing temperatures with snow to warm weather (approximately 80°F) on a building rooftop. The test in freezing conditions was aborted due to condensation of the instrument optics, and while this issue was addressed through modification, the subsequent (and final) field test was performed during temperate (non-freezing) weather conditions. The instrument appeared to perform without issue in non-freezing weather conditions, though the

results did not meet acceptable performance criteria (i.e., accuracy) for most of these tests.

- ***Ruggedness, User-Friendliness, Ease of Setup.*** The instrument was transported to test sites via truck (driven by the developer) or by air freight. The instrument did not appear to sustain any damage, and was set up and operated as expected. Setup required less than a few hours, and moves between locations within a site were completed in less time. In all cases, the instrument developer set up the instrument and was the only operator; therefore user-friendliness could not be determined.

Table 15 lists the performance criteria and whether they were achieved during the tests.

Table 15. Performance criteria and results.

Performance Objective	Metric	Success Criteria	Data Requirements	Notes	Objective Achieved?
Relative accuracy (bias)	Result compared to reference method	+/-20%	9 data pairs minimum at three levels	12 data pairs at three levels were collected	No
Two or more metals	Sb, As, Ba, Be, Cd, Co, Cr, Pb, Hg, Mn, Ni, Se, Ag, Tl	2 metals minimum	Instrument can be used as a CEMS only for metals that are tested	Cd, Cr, Ni, Pb, and Hg were monitored in this field test	Yes
CD	Difference in output of reference value after stated period of operation	Within 5%, measured once each day for 7 consecutive days	Measured once at the beginning and end of each test day using the medium concentration spike under regular test operating conditions	Instrument was checked at the beginning and end of each test day	No
Zero drift	Difference in output with zero input after stated period of operation	Within 5%, measured once each day for 7 consecutive days	Measured once at the beginning and end of each test day using the medium concentration spike under regular test operating conditions	Instrument was checked at the beginning and end of each test day	Yes
Response time	Amount of time instrument requires to respond to a steady state reading at least 95% of maximum	Less than 2 min	See note	For ABF-LIPS this is a near-instantaneous figure (milliseconds)	Yes

Table 15. Performance criteria and results (continued).

Performance Objective	Metric	Success Criteria	Data Requirements	Notes	Objective Achieved?
Calibration standard	A known amount of metal(s) delivered to the CEMS to determine response and drift	Performed at +/-20% of the applicable emission standard for each metal	Performed at the beginning (and end, for CD) of each day using the medium concentration spike under regular test conditions		Yes
Measurement location	Probe inlet should be in location with minimal turbulence or flow disturbance	At least 8 equivalent diameter distances downstream of any control device, bend, spike introduction, etc.	Will use existing ports	Existing ports are all within minimum requirement	Yes
RM measurement and traverse points	Location at least 8 equivalent diameters beyond flow disturbances, spike introduction, etc.	At least 8 equivalent diameter distances downstream of any control device, bend, spike introduction, etc.	Will comply with appropriate regulations (see note)	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.	Yes
Practical limit of quantitation	10× the SD at the blank level				Yes
Capability in various environments and conditions	Exposure to various climates and source operating conditions should not impact data quality	Measurements performed under varying weather conditions in outdoor locations within acceptable accuracy criteria	Operation/performance measurement in varying (outdoor) weather conditions	Tested at three separate geographic facilities, some outdoor, and various sources at some facilities	Difficulties in cold climates, otherwise performed reasonably well in various conditions

Table 15. Performance criteria and result (continued).

Performance Objective	Metric	Success Criteria	Data Requirements	Notes	Objective Achieved?
Ruggedness, user-friendliness, ease of setup	Time required for setup, operation learning, and troubleshooting	Measurements performed under varying weather conditions in outdoor locations within acceptable accuracy criteria	Ruggedness: Operation/performance measurement in varying (outdoor) weather conditions and following transportation. user - friendliness/setup ease: New users should become proficient within 3 days training.		Setup was less than one hr; only operator was developer so user friendliness/ease of setup was not measured.

4.3 PERFORMANCE ASSESSMENT

4.3.1 NADEP 2003

ABF-LIPS measurements for the Cr plating line exhaust and the electroless Ni line exhaust yielded unusable spectra for the three spiked metals of interest (Cr, Ni, Cd). This was likely due to an incorrect exposure time setting for the detector. It should be noted, however, that the two RMs used at the Cr plating line exhaust, USEPA 29 and 306, had poor agreement, with a RA beyond that allowed for new CEMS technologies (20%) per PS-10. The comparison for the two RMs is presented in Table 16.

Table 16. Comparison of two reference methods for Cr.

Chrome Plating Line (sampled after Enforcer III)			
Reference Method Results (mg/DSCM)	No Spike	Medium Spike	High Spike
Total Cr (USEPA Method 306)	0.00017	0.00012	0.00096
Total Cr (USEPA Method 29)	0.00068	0.0016	0.00069
% difference of Method 306	-75.0	-92.5	39.1

Results from the Kirksite furnace suggest that ABF-LIPS measurements are generally anticorrelated to the RM. Best-fit lines through the data, with R^2 values, are shown in Figures 27 through 29. Obviously, these R^2 values are poor, reflective of the poor data generated by ABF-LIPS at this site (i.e., the data appear random). Since this was the last of three sites measured during the NADEP tests, it is possible that the instrument had suffered some damage during transport and setup between sites. As such, RA for these data could not be calculated.

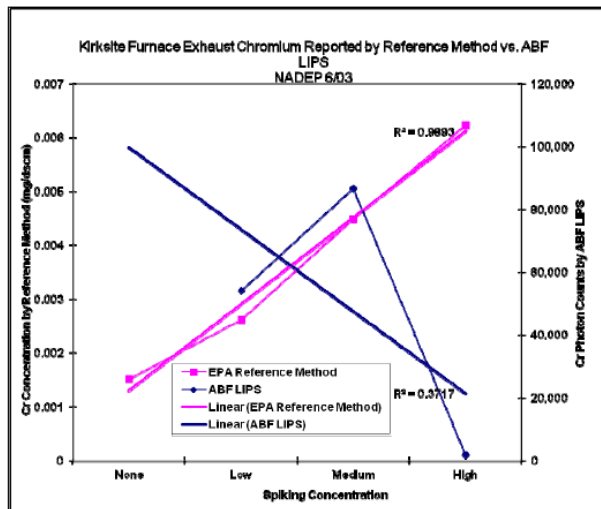


Figure 27. ABF-LIPS versus reference method result for Cr at Kirksite Furnace.

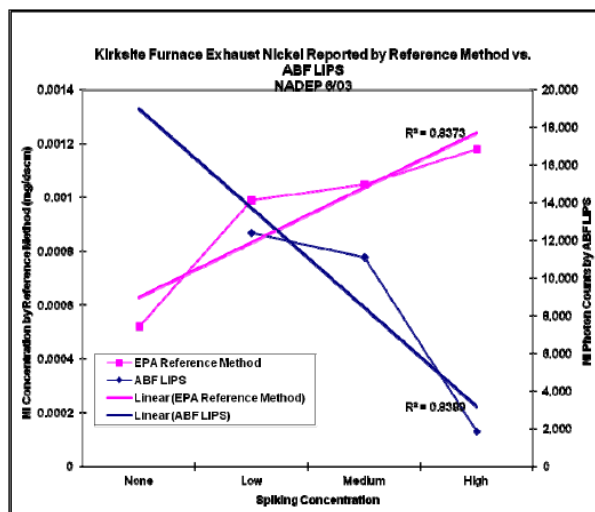


Figure 28. ABF-LIPS versus reference method result for Ni at Kirksite Furnace

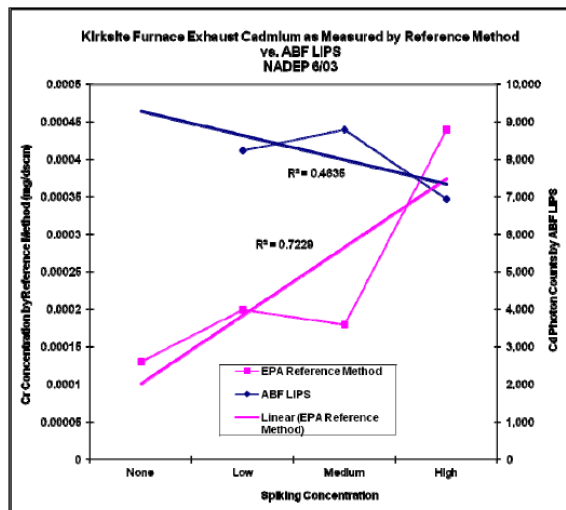


Figure 29. ABF-LIPS versus reference method result for Cd at Kirksite Furnace

4.3.2 TEAD 2005 Performance Assessment

The RA of ABF-LIPS to the RM for the TEAD September 2005 field test is presented in Table 17.

Table 17. Comparison of ABF-LIPS and reference method results from TEAD, September 2005.

Element	Measurement Method	Low Spike/ %RA	Std. Dev./ %Variance	Medium Spike	Std. Dev./ %Variance	High Spike	Std. Dev./ %Variance
Cr	USEPA Reference Method	5.7	2.6	2.8	1.5	148.4	12.0
Cr	ABF-LIPS	0.0	3.0	294.0	58.8	1279.0	383.7
Cr	%RA/ Ref. Method %Variance	>100%	46.5%	-99.0%	54.2%	-88.4%	8.1%
Ni	USEPA Reference Method	27.0	7.6	19.0	19.7	604.0	54.3
Ni	ABF-LIPS	11.0	3.5	1189.0	345.0	1458.0	452.0
Ni	%RA/ Ref. Method %Variance	145.5%	28.3%	-98.4%	103.8%	-58.6%	9.0%
Cd	USEPA Reference Method	61.1	39.1	30.6	8.1	141.3	26.2
Cd	ABF-LIPS	0.0	35.1	252.0	73.1	282.6	98.9
Cd	%RA/ Ref. Method %Variance	>100%	63.9%	-87.9%	26.5%	-50.0%	18.5%
Pb	USEPA Reference Method	375.3	104.5	204.1	67.4	224.6	44.9
Pb	ABF-LIPS	33.0	39.4	245.0	119.5	868.0	118.4
Pb	%RA/ Ref. Method %Variance	1037.1%	27.8%	-16.7%	33.0%	-74.1%	20.0%
Hg	USEPA Reference Method	184.8	38.0	189.4	105.9	363.2	600.3
Hg	ABF-LIPS	194.0	205.6	537.0	145.0	1016.0	274.3
Hg	%RA/ Ref. Method %Variance	-4.8%	20.6%	-64.7%	55.9%	64.3%	165.3%

Most runs did not pass the 20% RA criteria of PS-10. For example, the ABF-LIPS RA for Hg was 4.8%, 64.7%, and 64.3% for the low, medium, and high spike runs, respectively. However, the SDs of the RM were high as evidenced by the variances shown in the SD/variance columns of Table 17. The RM results for Cr, for instance, had variances of 46.5%, 54.2%, and 8.1% for the low, medium, and high spike runs, respectively. This variance may, in part, be the result of the residual metals in the furnace; runs conducted in the first day particularly showed a gradual decline in several metals, particularly Pb. These residual metals may have gradually burned off in the first several runs (the first four runs were low spike, followed by four runs of medium spike, then four runs of high spike over the three days of testing) but could have contributed to the high SDs in the RM results during the first two days of testing (the third day of testing, i.e., high spike runs, had the lowest SDs). It is also likely that the higher spike conditions were proportionately less influenced by the background burn-off of residual metals. Finally, much of the error could be the result of less-than-optimal spiking metal delivery which might have resulted in run-to-run variance in the amount of metals injected to the airflow.

Response times of ABF-LIPS are near instantaneous, and meet the PS-10 criteria for response time of less than 2 min.

The data presented in Table 17 are shown graphically in Figures 30 through 32.

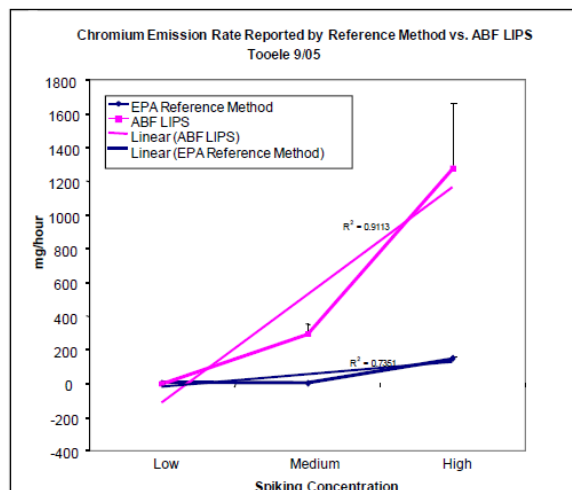


Figure 30. ABF-LIPS versus reference method for Cr at TEAD munitions deactivation furnace, September 2005

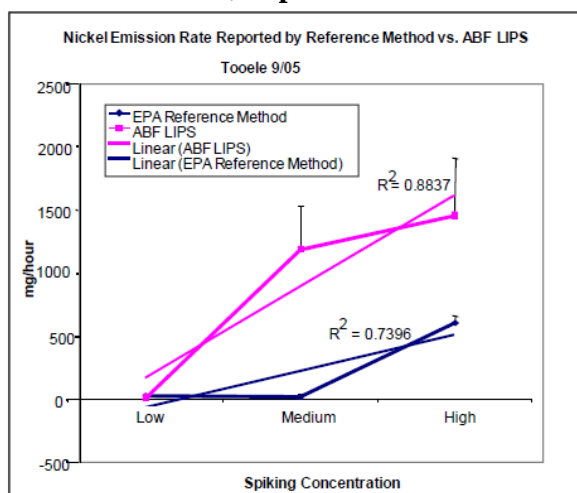


Figure 31. ABF-LIPS versus reference method for Ni at TEAD munitions deactivation furnace, September 2005

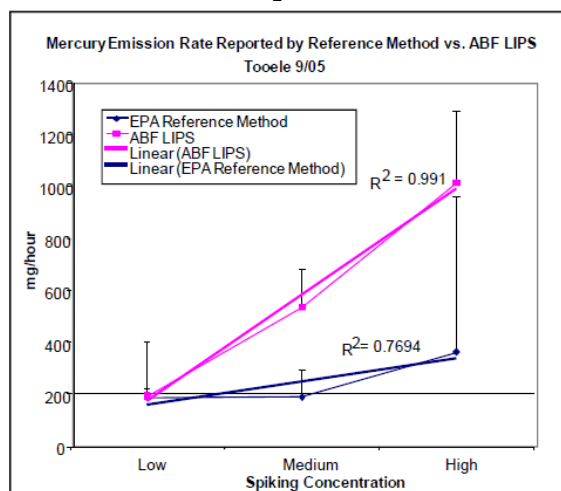


Figure 32. ABF-LIPS versus reference method for Hg at TEAD munitions deactivation furnace, September 2005

Zero calibration of ABF-LIPS was checked at the beginning and end of each test day. There were no peaks above the noise level in the emission spectra.

CD was determined by inspecting the ABF-LIPS results of the first run of each day at a given concentration with the last run of the day at that concentration. CD did not meet the 5% drift criteria of PS-10.

4.4 TECHNOLOGY COMPARISON

The standard method used in these studies as a RM (USEPA Method 29) requires a substantial labor effort involving at least two highly-trained individuals followed by substantial analytical work by an approved laboratory. Results are not obtained in real time—two weeks is a standard turnaround time. The sample gathering procedure using this method can also be quite dangerous, often requiring scaling of stacks by personnel.

ABF-LIPS was operated by one person with minimal setup. The equipment was not user friendly at this stage of development, but clearly was simpler from an operator perspective than that of the RM. Results were obtained in near real time, with only 2-min analysis cycles (versus the 80 to 120 min cycle times of the RM), though the emission spectra were not automatically converted to mass of a given metal in the version of the instrument and software used during the field tests. ABF-LIPS can be setup to remotely monitor a source, something the RM does not lend itself to. Further development of ABF-LIPS will allow remote operation, though the tested version required “hands-on” attention.

5.0 COST ASSESSMENT

5.1 COST REPORTING

Estimates for ABF-LIPS capital and operating costs are listed in Table 18. Since these are rough estimates, a range of costs are provided. Operating costs for ABF-LIPS are on an annual basis.

Table 18. Comparison of ABF-LIPS and reference method results from TEAD, September 2005.

ABF-LIPS Monitoring Costs							
Direct Environmental Activity Process Costs				Indirect Environmental Activity Costs (existing process – Method 29)		Other Costs (Existing Process Only)	
Start-Up		Operation & Maintenance					
Activity	\$K	Activity	\$K	Activity	\$K	Activity	\$K
Facility preparation, mobilization	10-250	Labor to operate equipment	10-20	Compliance audits (<i>for comparison</i>)	5	Overhead associated with process (<i>for comparison</i>)	2
Equipment design	5	Utilities	1-3	Document maintenance (<i>for comparison</i>)	2	Productivity/Cycle time (<i>for comparison</i>)	0
Equipment purchase	65-150	Consumables and supplies	1-2	Environmental Management Plan development & maintenance (<i>for comparison</i>)	5	Worker injury claims & health costs (<i>for comparison</i>)	0
Installation	20-40	Equipment maintenance	2-10	Reporting requirements (<i>for comparison</i>)	3		
Training of operators	5-10	Training of operators	0	Test/analyze waste streams (<i>existing process only</i>)	40		

Besides the cost of the ABF-LIPS instrument, the highest capital cost item is facility preparation. Since weather proved to be an issue during the tests, it is likely that a structure will have to be built to house the unit. In certain applications (outdoor on a stack, for instance), the structure will need to be more robust, with climate controls such as a heater and air conditioner. Beyond the one-time capital costs, an operator must tend to the instrument; these costs are given on an annual basis. Most sites which have personnel operating the processes can incorporate ABFLIPS as another process unit at marginal cost, estimated to be \$10,000 to \$20,000 per year.

5.2 COST ANALYSIS

5.2.1 Major Component Costs

These include the high-power laser, the intensified charge couple array, and the spectrograph. The total for these three components is approximately \$150,000, which provides wide-ranging

capability in detecting metal-laden aerosols in near real time. These costs are based on the manufacturer's prices for these components.

It will not be necessary for most users to have the capability of detecting every element on the periodic table. Thus, it is feasible to develop a "site-specific" ABF-LIPS system at a substantially reduced cost compared to the current ABF-LIPS system. Such a site-specific system would reduce the cost to about \$65,000 for four elements. The major saving by manufacturing a site-specific ABF-LIPS comes from the elimination of a detector costing \$80,000 to \$85,000 and replacement with a gateable photomultiplier tube plus a narrowband notch filter for an element.

5.2.2 Minor Component Costs

These include the aerosol sampling and focusing unit and comprise a cost on the order of \$7000.

5.2.3 Software Cost

Software comprises a relatively small cost. Current software was written by researchers at ORNL. Development of ABF-LIPS into a commercial version will require a more "userfriendly" version of the software. The typical cost for commercial software for an instrument such as the ABF-LIPS is approximately \$5000 to \$8000 a copy.

5.3 COST COMPARISON

Annual sampling of a stack source such as the furnace at TEAD costs \$57,000 but does not require a capital cost. Capital costs for an ABF-LIPS system capable of measuring multi-metals (all HAP metals) is \$190,000 to \$455,000. Annual O&M costs for ABF-LIPS are projected to be \$14,000 to \$35,000. Assuming the useable life of an ABF-LIPS unit is 10 years, the annualized cost is \$33,000 to \$80,500 (annual O&M + startup cost/10). Thus, ABF-LIPS could save up to \$24,000/year, which does not consider the eventual regulatory requirement of a CEMS or the possible alternative of more frequent traditional sampling, as well as improved process control. If the DoD has 200 such sites where ABF-LIPS can be implemented, the total cost savings then could be up to \$4.8M/year. Other installations, requiring more robust climate control, could cost up to \$23,500 more per year for ABF-LIPS.

6.0 IMPLEMENTATION ISSUES

6.1 COST OBSERVATIONS

Projected annual costs for ABF-LIPS assume continued development of the instrument to result in an accurate, user-friendly unit. Additional development beyond 2 to 3 years, together with inflation, could result in increased cost of the unit. The possible increased cost would be more than offset by increased monitoring costs to comply with CEMS regulatory requirements using traditional methods, if and when those regulations are implemented. In that case, annual monitoring costs could be expected to at least double and likely increase several multipliers beyond current annual monitoring costs.

6.2 PERFORMANCE OBSERVATIONS

The ABF-LIPS prototype tested during each of the three field tests were progressively more compact and simpler to set up and operate; however, in all tests significant observation and adjustments by the developer were required. Only the developer operated the instrument at all three tests, so the ease of which others could operate was not determined. The tests at NADEP showed that the unit is extremely sensitive to parameter settings, which have not yet been completely resolved. The performance at the third field test was much improved, though PS-10 criteria were not met.

6.3 SCALE-UP

Not Applicable

6.4 OTHER SIGNIFICANT OBSERVATIONS

The existing ABF-LIPS prototype is currently not weather-resistant, and must be housed indoors in a temperature-controlled environment. Further development of the instrument might produce a unit that can be housed in a weather-tight enclosure, but this will likely entail additional cost. Since most source measurement locations are after pollution control equipment and on a stack (outdoor), a separate structure with climate control will have to be built for such applications. This was not included in cost considerations, but may be expected to add \$20,000 to capital costs, and additional O&M charges for electric.

While ABF-LIPS is significantly simpler than the RM sampling and analysis, a trained operator will still be required for occasional operation, maintenance and trouble-shooting. Some facilities may not have workforce availability, which could further add to costs. Additionally, until the units are widely in operation, servicing may require that the unit be non-operational for an extended period since few service centers would be available.

Changes to the process may result in altered matrix interference properties, requiring recalibration of the system. Matrix interference includes any component of the sample, such as particulate, which may interfere with detection of the target metals. Some matrix interference may be severe enough to limit the minimum detection level to unacceptable levels. As an example, a change in feedstock in a munitions DF, or a change to the emission control system,

might alter the amount of soot C in the flue gas. This could affect the sensitivity of the detector due to absorption, which would necessitate recalibration. Also, particle size variations as a result of process or feed changes may require that the system be re-calibrated, and some particle size distributions may result in unacceptably high minimum detection levels.

Lastly, minimum detection levels for ABF-LIPS are not as good as traditional solution techniques. Concentrating the feed stream via other methods such as cryogenic trapping and flash-heating are possible, but will add to system cost.

6.5 LESSONS LEARNED

Reliable spiking of the airstream with metals proved to be a challenge. Based on RM results, it is unclear whether delivery of the spiking aerosol is reproducibly accurate. Further, RM testing was, in many cases, beyond the 20% required of PS-10.

6.6 END-USER ISSUES

The DoD has assigned a high priority to this area under the Navy's Environmental Quality Research and Development Requirement 2.II.02.b "Improved Field Analytical Sensors, Toxicity Assays, Methods, and Protocols to Supplement Traditional Sampling and Laboratory Analysis," the Air Force's requirement for "New Technology to Meet Clean Air Act Amendments Monitoring Requirements for Toxic Release Inventory Compounds," and the Army's requirement for "Hazardous Air Pollutant and Volatile Organic Compounds Emission Control."

The following factors may limit or complicate integration of ABF-LIPS into existing operations:

System cost. Currently-available commercial CEMS are in the \$200,000 range. Depending on the number, type, and physical arrangement of stacks at a facility, the cost of monitoring by CEMS may be multiplied. In addition, consumables and maintenance costs may translate into O&M costs that exceed capital expenditures over some years.

Downtime for installation, testing and maintenance/repairs. Facilities may need to be taken offline temporarily for fitting CEMS. In addition, malfunction of CEMS may require an operation going offline. It may be possible to revert to manual (i.e., Method 29) sampling and analysis during CEMS repairs.

Physico-chemical Properties of Aerosols. Larger particles (particle diameter $[D_p] > 10 \mu\text{m}$) may not be collected effectively by the sampling nozzle, while small particles ($D_p < 50 \text{ nm}$) may be lost by diffusional transport to the sampling system before they are detected.

Non-uniform or changing air stream patterns in stack not suitable for point source monitoring. Some stacks have very non-uniform flow patterns (e.g., vortexes) which do not lend themselves well to point sampling (the typical method for CEMS). These sources may require development of automated path CEMS sampling.

Very high levels of one metal that can saturate the signal-to-noise ratio of other metals at lower levels. For example, Pb in a munitions DF may result in swamping of the signal of other HAPs.

This may be overcome by making adjustments to the analysis software or may require hardware modifications. The instrument manufacturer would most likely have to take care of such an adjustment, and this cost has been considered in the estimate above.

Extreme environments. High temperature and high humidity can decrease equipment life and operating performance. A temperature-controlled superstructure or advanced cooling system may be required in such cases. Recommended environmental operating conditions will be developed for a base instrument. In climates where freezing weather occurs a housing structure with climate control will be necessary.

In order to transition this technology, a private company that has the capability to manufacture and market this technology has been identified, Comstock, Inc. Comstock, Inc., will be involved in the development and engineering of the hardware/software and in commercialization of this technology. USEPA has agreed to become a stakeholder on this project. USEPA will review the test/demonstration plans for the project and will be onsite during the field tests to ensure compliance with the performance specifications and method validations. These validations will help to ensure that the technology is transitioned to the air monitoring community. Also, the transitioning of the ABF-LIPS technology to the numerous DoD activities that could use this technology will be accomplished through the publication of articles, the distribution of videos and pamphlets, the presentation of test results at conferences, the incorporation into the joint service pollution prevention library, and Web page development by the performers of this proposal.

The main concern with the ABF-LIPS is the high cost of the capital equipment. In order to make the instrument more competitive with traditional source test equipment, a single element version of the ABF-LIPS can be produced. This will significantly reduce capital costs, though limiting the use of that particular instrument to its intended application.

6.7 APPROACH TO REGULATORY COMPLIANCE AND ACCEPTANCE

In 1990, Congress amended Section 112 of the Clean Air Act requiring the USEPA to identify and regulate all significant stationary sources that emit any of 189 HAPs. Eleven of these HAPs are metals (Sb, As, Be, Cd, Cr, Co, Pb, Mn, Hg, Ni, and Se). Currently, the USEPA has a list of 173 source categories and is issuing regulations requiring these sources to use maximum available control technology to reduce HAP emissions. The USEPA is developing regulations to limit emissions of the HAP metals from sources such as incinerators and coal-fired power plants, among others. The DoD possesses or controls many such assets which would be subject to these regulations. Continuous emissions monitoring of toxic metals has been proposed by the USEPA (USEPA/625/R-97/001, 1997) and included in the CFR (40 CFR Parts 72 and 75) for use at facilities that emit HAPs. Further, CEMs are required under some of the USEPA regulations for either continual compliance determinations or determination of exceedances of the standards. Instruments such as ABF-LIPS can measure metals in real-time, but require validation using USEPA approved methods. Further development of ABF-LIPS will be required, however, prior to additional validation testing and eventual regulatory acceptance.

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APPENDIX B

PERFORMANCE SPECIFICATION 10 (PS-10)

PERFORMANCE SPECIFICATIONS FOR MULTI-METALS CEMS

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 2 specifications: 40 CFR part 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 specification) 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

The total equipment required for the determination of metal concentration. The system consists of the following major subsystems:

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.

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

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

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% 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% 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% 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% 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% 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.

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.

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, Section 2.2 and 2.3.

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% of the path within the inner 50% of the stack or duct cross sectional area, or (3) be centrally located over any part of the centroidal area.

3.2 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% 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% of the high level value.

4.2 RELATIVE ACCURACY (RA)

The RA of the CEMS must be no greater than 20% of the mean value of the RM test data in terms of units of the emission standard for each metal, or 10% 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% of the emission standard for each metal. The calibration shall be performed at a point equal to 80 to 120% 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 (ZD) for each metal. If this is not possible or practicable, the design must allow the ZD determination to be made at a low level value (zero to 20% of the emission limit value). The CEMS zero point for each metal shall not drift by more than 5% 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 min to achieve 95% 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 Section 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 hr. 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 5 min, whichever is less.

5. PERFORMANCE SPECIFICATION TEST PROCEDURE

5.1 PRETEST PRUSEPARATION

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 CD and ZD once each day (at 24-hr 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-hr 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% of normal load, or as specified in the applicable subpart.

6.0 THE CEMS CALIBRATION AND ZD 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-min 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% of the emission limit) for one of the metals which will be monitored, or for Fe. If Fe 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) or 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 (O₂) 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 3/22/95 there is no approved alternative RM (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) to Method 29.

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 SD 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:

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

where n is equal to the number of data points.

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 SD

Calculate the SD of a data set as follows:

$$SD = \sqrt{\frac{\sum x_i^2 - \frac{1}{n}(\sum x_i)^2}{n-1}}, \quad (5)$$

8.3 RELATIVE ACCURACY (RA)

Calculate the RA as follows:

$$RA = \frac{\bar{d} + \frac{t_{0.975}SD}{\sqrt{n}}}{\overline{R_{REM}}}, \quad (6)$$

where $\bar{d}$ 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 SD calculated according to Equation 5, $\overline{R_{REM}}$ 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% 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	3.365	13	2.179
4	3.182	9	2.306	14	2.16
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 or 7% 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. USEPA, Contract No. 68-D2-0164 (4/25/94).

APPENDIX C

STACK SAMPLING FIELD NOTES

PES, Inc.	Metals Calculations		
Plant	Tooele Army Depot		
Project #	1111.001		
Operation	Burnoff Kiln		
Run	TAD-4		
Location	Baghouse Exhaust		
Date	10/26/2004		
INPUTS			
Vlc =	53.4	cc	Vol. Of H ₂ O collected (impingers)
Vm =	62.25	cf	Dry gas meter reading
Pb =	24.8	in. Hg	Barometric pressure
Ps =	24.78	in. Hg	Stack pressure
dP ^{0.5} =	0.505		Average sq. rt. delta P
dH =	1.81	in. H ₂ O	Average delta H reading
Tm =	52.8	F	Average meter temperature
Ts =	388.6	F	Average stack temperature
Dn =	0.322	in.	Nozzle diameter
Y =	1.007		Meter calibration factor
t =	80	min.	Duration of sampling time
A =	2.18	sq.ft.	Cross sectional area of stack
Cp =	0.84		Pitot tube coefficient
Kp =	85.49		Pitot tube constant
K1 =	17.64	R/in.Hg	constant
K2 =	0.04707	cu.ft/ml	constant
K3 =	0.002669	in.Hg-cf/ml-R	constant
[O ₂] =	17	%	(Assumed)
[CO ₂] =	3	%	N ₂ = 100 – (CO ₂ + O ₂)
			duct diameter (in):
		0.833	9.996339

Tooele Army Depot	Baghouse Exhaust		
Run #	TAD-4		
Page 2			
CALCULATIONS			
1) Volume of gas sampled at standard conditions, Vmstd			
$V_{mstd} = K_1 * Y * V_m * (P_b + dH/13.6)/T_m$			
Vmstd =	53.77	cu.ft	
	1.52	cu.m	
2) Volume of water vapor collected at standard conditions.			
$V_{w(std)} = K_2 * V_{lc}$			
Vw(std) =	2.51	scf	
3) Decimal fraction of moisture by volume in stack gas			
$B_{ws} = V_{wstd}/(V_{mstd} + V_{wstd})$			
Bws =	0.045		
4) Molecular weight of the stack gas on a wet basis Ms.			
$M_s = (1 - B_{ws}) * ((44 * \%CO_2) + (32 * \%O_2) + (28 * \%N_2)) + (18 * B_{ws})$			
Ms =	28.63		
5) Average stack gas velocity.			
$V_s = K_p * C_p * (dP^{0.5}) * (T_s / (P_s * M_s))^{0.5}$			
vs =	39.63	ft/sec	
6) Average actual stack gas volumetric flowrate.			
$Q = 60 * v_s * A_s$			
Q =	5183	cfm	
	146.79	cmm	

Tooele Army Depot		Baghouse Exhaust	
Run #	TAD-4		
Page 3			
7) Average stack gas dry volumetric flowrate.			Tstd = 68oF
$Q_{std} = Q * (T_{std}/T_s) * (P_s/P_{std})$			Pstd = 29.92 in. Hg
Qstd =	2552	DSCFM	
	72.28	dscmm	
8) Analytical data			
Metals Concentrations			
Nickel			
C(Ni)1 =	0.0002	mg/l Concentration of Ni in charge blank	
V(1) =	0.133	l Volume of charge	
m(Ni)1 =	0.000027	mg Total Ni in charge blank	
C(Ni)2 =	0.0002	mg/l Concentration of Ni in wash blank	
V(2) =	0.162	l Volume of wash	
m(Ni)2 =	0.000032	mg Total Ni in wash blank	
m(Ni)3 =	0.00027	mg Total Ni in filter blank	
m(Ni)4 =	0.068	mg Total Ni in sample	
m(Ni)5 =	0.00033	mg Total Ni in sample blank	
m(Ni)6 =	0.06767	mg Total Ni net	
[Ni] =	0.04444	mg/DSCM (m(Ni)6/Vmstd)	
E =	192.73	mg/hr	

Tooele Army Depot		Baghouse Exhaust	
Run #	TAD-4		
Page 4			
Cadmium			
C(Cd)1 =	0.0002	mg/l Concentration of Cd in charge blank	
V(1) =	0.133	l Volume of charge	
m(Cd)1 =	0.000027	mg Total Cd in charge blank	
C(Cd)2 =	0.0002	mg/l Concentration of Cd in wash blank	
V(2) =	0.162	l Volume of wash	
m(Cd)2 =	0.000032	mg Total Cd in wash blank	
m(Cd)3 =	0.00003	mg Total Cd in filter blank	
m(Cd)4 =	0.035	mg Total Cd in sample	
m(Cd)5 =	0.00009	mg Total Cd in sample blank	
m(Cd)6 =	0.03491	mg Total Cd net	
[Cd] =	0.022926	mg/DSCM (m(Cd)6/Vmstd)	
E =	99.43	mg/hr	
Chromium			
C(Cr)1 =	0.001	mg/l Concentration of Cr in charge blank	
V(1) =	0.133	l Volume of charge	
m(Cr)1 =	0.000133	mg Total Cr in charge blank	
C(Cr)2 =	0.001	mg/l Concentration of Cr in wash blank	
V(2) =	0.162	l Volume of wash	
m(Cr)2 =	0.000162	mg Total Cr in wash blank	
m(Cr)3 =	0.00086	mg Total Cr in filter blank	
m(Cr)4 =	0.015	mg Total Cr in sample	
m(Cr)5 =	0.00116	mg Total Cr in sample blank	
m(Cr)6 =	0.01385	mg Total Cr net	
[Cr] =	0.009092	mg/DSCM (m(Cr)6/Vmstd)	
E =	39.43	mg/hr	

Tooele Army Depot		Baghouse Exhaust	
Run #	TAD-4		
Page 5			
Lead			
C(Pb)1 =	0.0002	mg/l Concentration of Pb in charge blank	
V(1) =	0.133	l Volume of charge	
m(Pb)1 =	0.000027	mg Total Pb in charge blank	
C(Pb)2 =	0.0002	mg/l Concentration of Pb in wash blank	
V(2) =	0.162	l Volume of wash	
m(Pb)2 =	0.000032	mg Total Pb in wash blank	
m(Pb)3 =	0.00013	mg Total Pb in filter blank	
m(Pb)4 =	0.0051	mg Total Pb in sample	
m(Pb)5 =	0.00019	mg Total Pb in sample blank	
m(Pb)6 =	0.00491	mg Total Pb net	
[Pb] =	0.003225	mg/DSCM (m(Pb)6/Vmstd)	
E =	13.99	mg/hr	
Mercury			
C(Hg)1 =	0.00004	mg/l Concentration of Hg in HNO3/H2O2 charge blank	
V(1) =	0.133	l Volume of charge	
m(Hg)1 =	0.000005	mg Total Hg in charge blank	
C(Hg)2 =	0.000055	mg/l Concentration of Hg in HNO3 wash blank	
V(2) =	0.162	l Volume of wash	
m(Hg)2 =	0.000009	mg Total Hg in wash blank	
C(Hg)3 =	0.000014	mg/l Concentration of Hg in KMNO4 charge blank	
V(1) =	0.151	l Volume of charge	
m(Hg)3 =	0.000002	mg Total Hg in charge blank	
C(Hg)4 =	0.000023	mg/l Concentration of Hg in H2O wash blank	
V(2) =	0.087	l Volume of wash	
m(Hg)4 =	0.000002	mg Total Hg in wash blank	

Tooele Army Depot		Baghouse Exhaust		
Run #	TAD-4			
Page 6				
Mercury (cont'd)				
m(Hg)5 =	0.00001	mg Total Hg in filter blank		
m(Hg)6 =	0.04905	mg Total Hg in sample		
m(Hg)7 =	0.00003	mg Total Hg in sample blank		
m(Hg)8 =	0.04902	mg Total Hg net		
[Hg] =	0.032193	mg/DSCM (m(Hg)8/Vmstd)		
E =	139.62	mg/hr		
9) Isokinecity				
An =	0.00057	ft^2	Area of nozzle orifice	
$\% I = 100 * Ts * ((K3 * Vlc + (Vm * Y / Tm) * (Pb + dH / 13.6)) / (60 * t * Ps * vs * An))$				
% I =	101.6			
Tooele Army Depot		Test Date	10/26/2004	
Baghouse Exhaust		Barometer	24.8	in.Hg
		Run #	TAD-4	
		Static P	-0.21	in.H2O
		Pitot Cp	0.84	
		Nozzle	0.322	

Sample	Delta-P	Stack Temp.	Delta H	Gas Meter Temp		(dP)^.5	velocity
Time	(in. H ₂ O)	(°F)	(in. H ₂ O)	IN	OUT		ft/sec
B-1	0.2	392	1.4	47	46	0.447	35.19
2	0.25	399	1.8	49	45	0.5	39.51
3	0.27	403	1.9	50	46	0.52	41.15
4	0.27	398	1.9	52	46	0.52	41.03
5	0.28	396	2	53	46	0.529	41.74
6	0.26	383	1.8	54	47	0.51	39.91
7	0.3	374	2.1	56	48	0.548	42.65
8	0.3	364	2.1	56	48	0.548	42.39
9	0.24	377	1.7	56	49	0.49	38.21
10	0.2	376	1.4	56	50	0.447	34.86
A-1	0.27	373	1.9	53	50	0.52	40.43
2	0.27	397	1.9	55	53	0.52	41.01
3	0.3	395	2.1	57	52	0.548	43.18
4	0.3	395	2.1	57	52	0.548	43.18
5	0.3	395	2.1	59	52	0.548	43.18
6	0.25	392	1.8	60	53	0.5	39.35
7	0.25	391	1.8	60	53	0.5	39.32
8	0.23	390	1.6	61	54	0.48	37.7
9	0.2	393	1.4	62	54	0.447	35.21
10	0.18	388	1.3	59	54	0.424	33.31
		388.6	1.81	55.6	49.9	0.505	39.63
				Avg.	52.8		

APPENDIX D

ABF-LIPS SPECTRA COLLECTED AT NADEP FIELD TEST, 2003

Averaged data for Chromium-Plating Site (Cr Site), NADEP

Spectra were analyzed after the field test and it was discovered that the detector, set to take as many data points as possible, was not parameterized correctly for timing sequence. Follow-up spectral analysis could not provide useful signals for identification and quantification of the three elements.

Averaged data for Nickel-Plating Site (Ni Site), NADEP

The baseline measurement from this site showed low concentrations of target elements, Ni, Cr, and Cd. The signal-to-noise ratios were near 2 for these 3 elements (1.96 for Ni at 351.5 nm, 1.74 for Cr at 425.5 nm, and 1.86 for Cd at 734.7, no signal at 537.8 nm) indicating their abundances were low, near the instrument detection limits. Based on the averaged spectrum for the baseline measurements at the 12 points (total of 65 spectra), Fe, C, and possibly Ti appear to be abundant in the emissions. The Ti lines are close to Fe in most cases making it difficult to separate from Fe. C could be from some polymer compounds used in the processes. There were possibly more elements than these 3, but the signal-to-noise ratios were low.

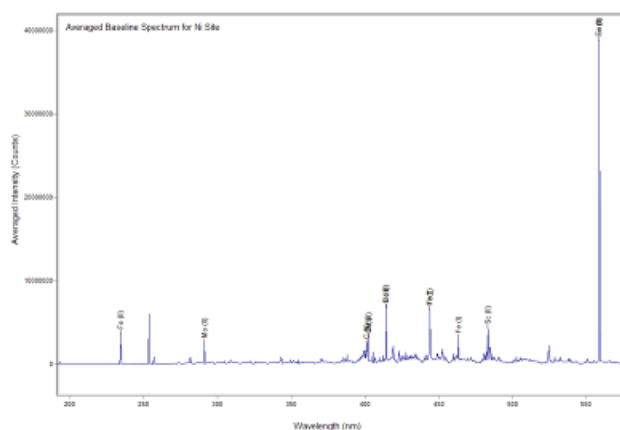


Figure 13. Averaged spectrum of the baseline emissions at the Ni site.

Major elements identified are also shown in the figure. No major peaks found beyond 600-nm wavelength, which region is excluded from the figure.

The signal-to-noise ratios were not adequate to enable a positive identification of the three elements for the three spiking runs at the Ni site. The spectra appear to have been collected with an incorrect exposure time. They were all observed at a delay time of 7 μ s and variable gate widths ranging from 10 to 50 μ s. The gate width appears to have little effect on the spectra; the delay time has some effect but not significant. It is possible an incorrect (too short) exposure time was used considering the results obtained later from Kirksite furnace. No record of the exposure time was taken, however.

Analysis for the Kirksite furnace exhaust, NADEP

Baseline Condition – The following plots in Figures 4 and 5 show the broadband spectra of the species observed by ABF-LIPS at the Kirksite under baseline condition (no metal spiking). The system parameters for the baseline-condition measurements remained unchanged throughout the 120-min sampling interval. The delay time for detection was set at 7 μ s after the laser pulse trigger arrived, while the shutter gate width was at 25 μ s. The flash lamp energy was 11.5 J and the electrical voltage setting was 2400 VDC.

The x-axis, the wavelength axis, ranges from 180 to about 900 nm. The limit of the y-axis is kept constant for all plots so comparison among the plots was possible. The peak height is used to indicate the abundance of the metal species present in the observed aerosol particles. Each plot in Figure 4 was obtained from averaging at least 5 ABF-LIPS measurements. This means that at least 5 data points (spectra) were taken by ABF-LIPS in each 20-min interval and the probe remained at a single point during each 20-min interval. In Figure 5, the 6-point averaged figure is an average of Figure 4-1 through 4-6. Also shown in the figures are the characteristic wavelengths of the target elements (Ni, Cd, and Cr) in the baseline emissions, per the National Institute of Science and Technology (NIST) atomic spectra library.

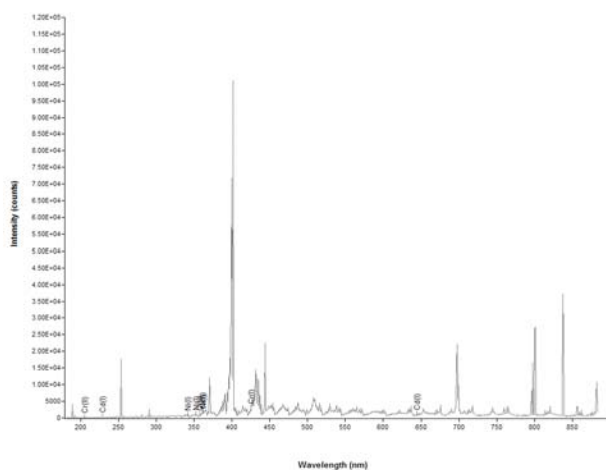


Figure 4-1

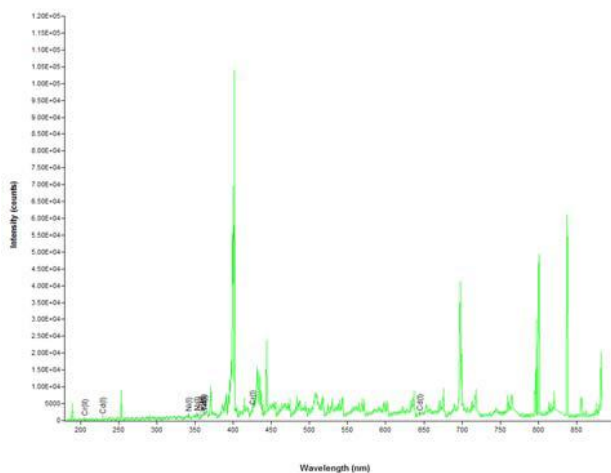


Figure 4-2

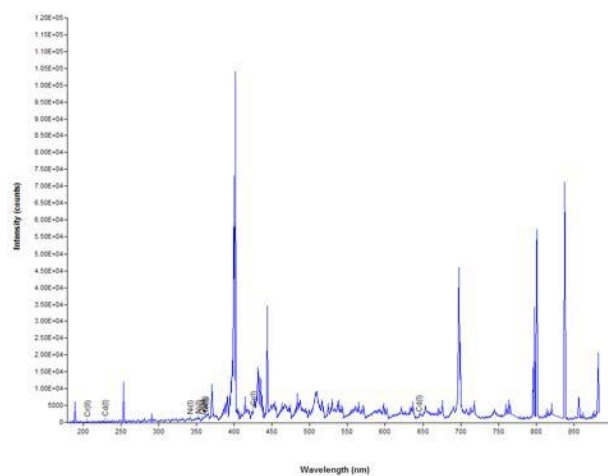


Figure 4-3

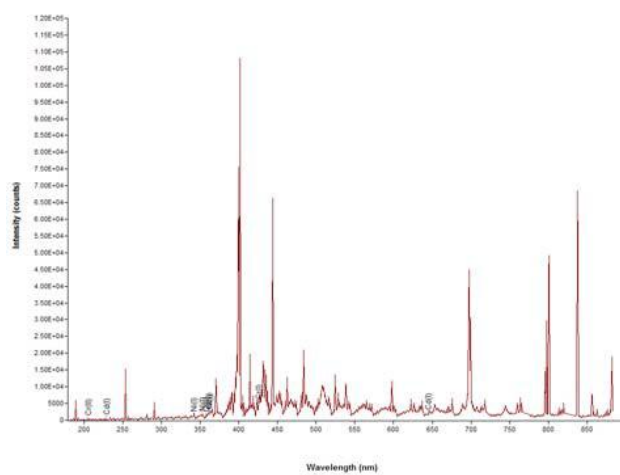


Figure 4-4

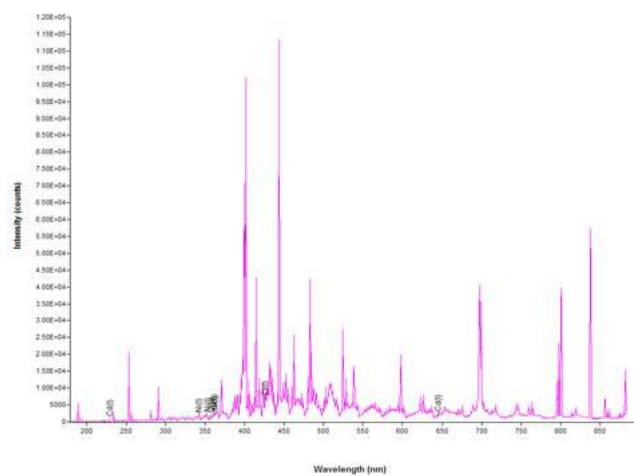


Figure 4-5

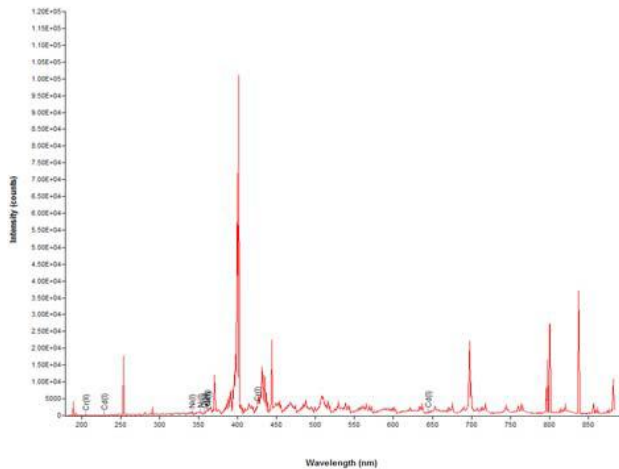


Figure 4-6

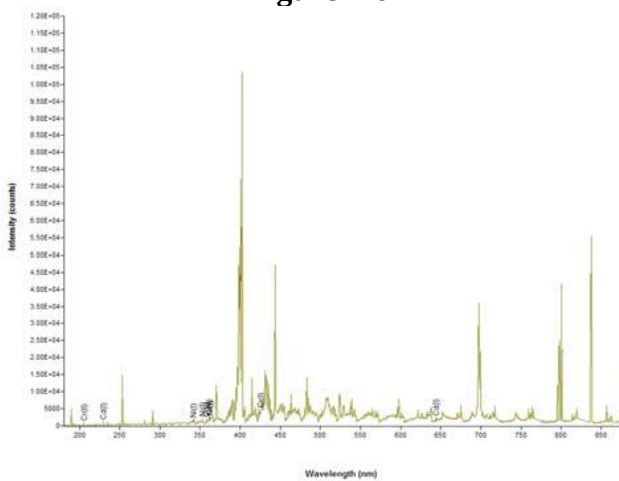


Figure 5. A 6-point averaged spectrum.

The spectra shown in Figure 4-1 through 4-6 suggest that at any of the 6 ABF-LIPS probe locations, the observed abundance of target elements, Ni, Cd, and Cr, were reasonably low based on the corresponding peak heights. The differences in the peak heights of the spectra suggest that the flow is not evenly distributed across the duct at the sampling point, or that the concentration of metals varied with time.

Several significant peaks between 430 to 550 nm are visible in Figures 4-4 and 4-5, but are relatively insignificant in the other 4 figures. The three target elements do not have strong emission lines in this wavelength window. Figures 6-1 through 6-6 show the expanded window view from 430 to 550 nm for each point in the duct cross section. The vertical limit of the Y-axis was kept constant in all 6 plots to enable easy comparison. The largest peak is located at 443.8 nm, which is characteristic of vanadium, V (I), at 7 μ s delay time. A weaker vanadium line, V (I), was also found at 483.3 nm. This weaker line is clear in Figures 6-4 and 6-5, but not in the other plots. The peak at 463.28 nm also exhibited the same pattern as the 443.8 nm in that the peak height started from a minimum and increased as the probe moved away from the duct wall. The peak height reached the largest value at point 5, then dropped to the minimum at point 6.

It is obvious that the distributions of the chemical species, as reflected in the identified peak heights, exhibited a pattern (i.e., not statistically similar) suggesting that it is possible that the flow or the fluid velocity across the duct cross section was significantly non-uniform. Based on the data, the maximum velocity is likely to be near point 5.

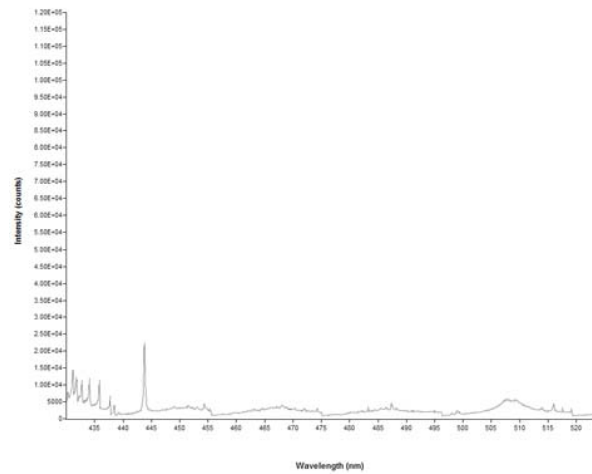


Figure 6-1. A spectrum between 430nm and 550 at point 1.

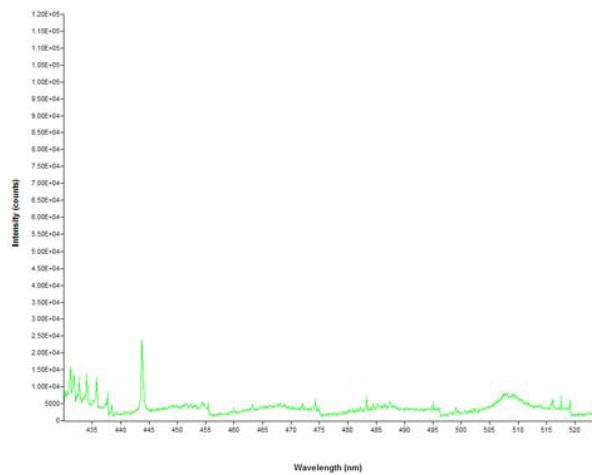


Figure 6-2. A spectrum between 430nm and 550 at point 2.

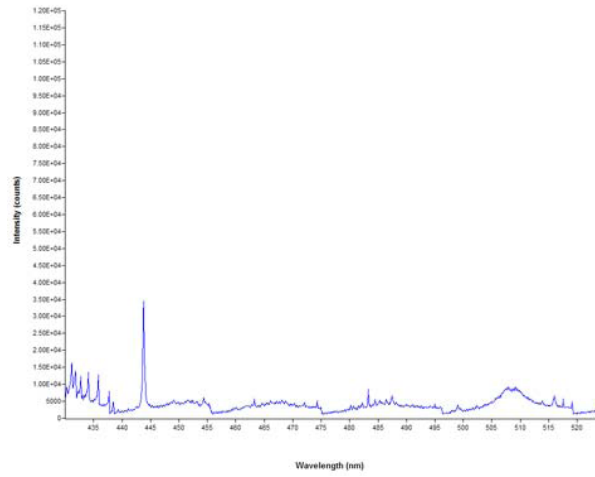


Figure 6-3. A spectrum between 430nm and 550 at point 3.

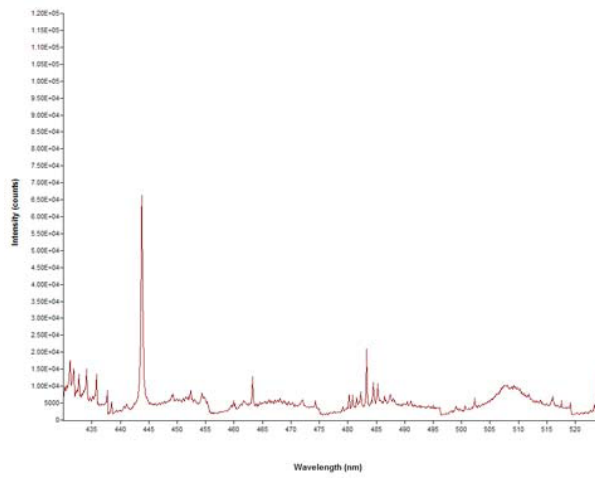


Figure 6-4. A spectrum between 430 nm and 550 at point 4.

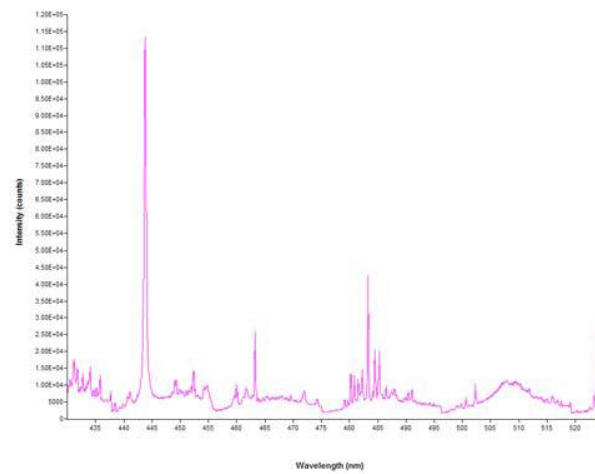


Figure 6-5. A spectrum between 430 nm and 550 at point 5.

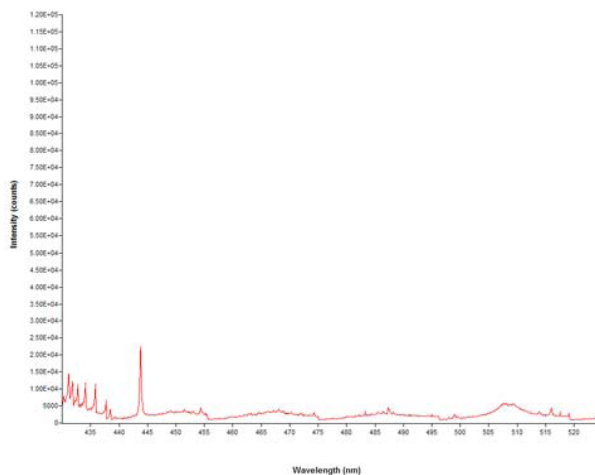


Figure 6-6. A spectrum between 430 nm and 550 at point 6.

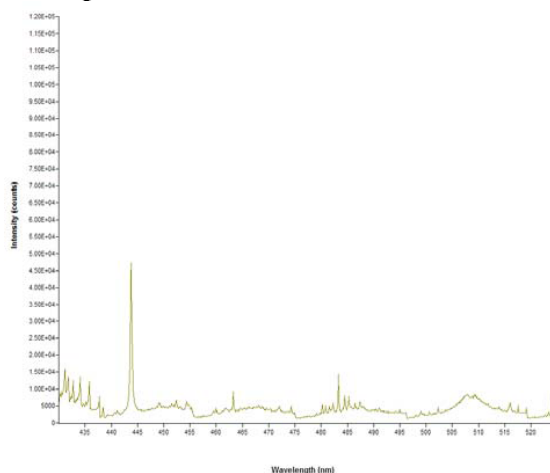


Figure 7. An averaged spectrum for the window between 430 nm and 550.

Low Spike Condition – The baseline emissions were spiked with the L (low concentration) solution which contained 330 μ g/L of Ni, 150 μ g/L of Cr, and 153 μ g/L of Cd. A 6-point test configuration was used for these runs, with 12 minutes at each point for a total of 72 minutes per run. There was a minimum of 3 points taken by ABF-LIPS at each probe location. Figure 8-1 through 8-6 are the broadband results with baseline (Figure 5) subtracted. Thus, any peaks shown in these figures would have resulted from the spiking solutions. However, it is important to note that due to variability in the baseline measurements a constant subtraction may not be appropriate for all data.

The non-uniformity of flow can be seen in Figures 8-1 through 8-6, where the peak intensities increased from point 1 in Figure 8-1 to point 6 in Figures 8-6. These figures provide a qualitative view of the problem from a spectroscopic point of view based. If the flow rate increased (flow velocity increased), then the amount of the analyte would increase, which could explain the large peaks seen in Figures 5 and 6. Thus, the cross-sectional distribution of chemical species at the Kirksite appears to be skewed toward points 5 and 6, based on the baseline corrected data.

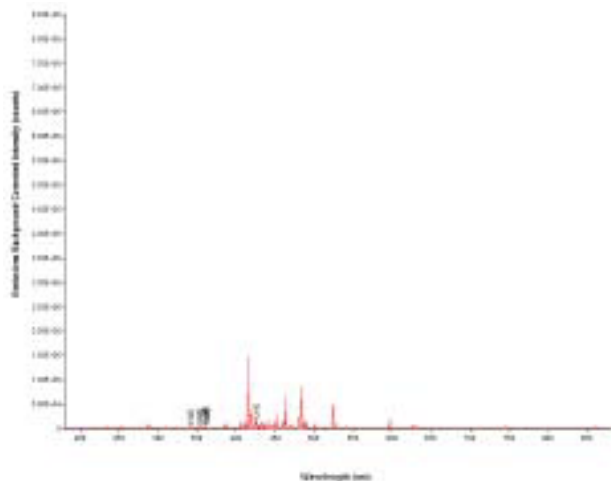


Figure 8-1. A broadband view of the ABF-LIPS spectrum at point 1.
Also marked are the three target elements, Ni, Cd, and Cr. Most of the strong lines (i.e., wavelengths) of these 3 metals are found in between 300 to 500 nm as shown.

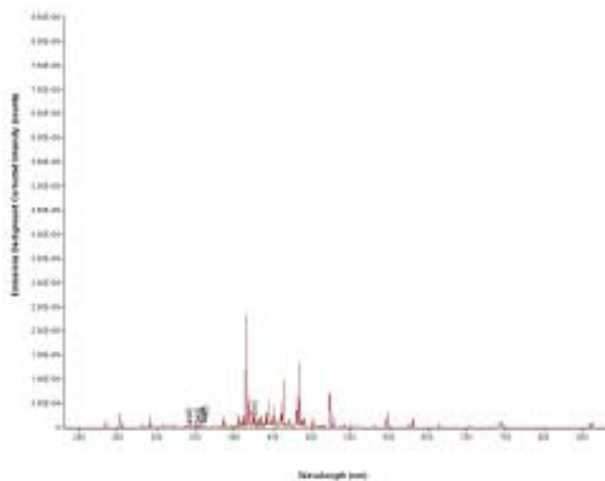


Figure 8-2. A broadband view of the ABF-LIPS spectrum at point 2.

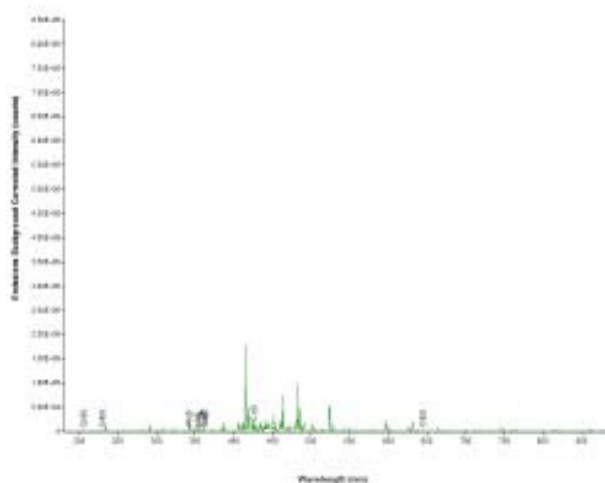


Figure 8-3. A broadband view of the ABF-LIPS spectrum at point 3.

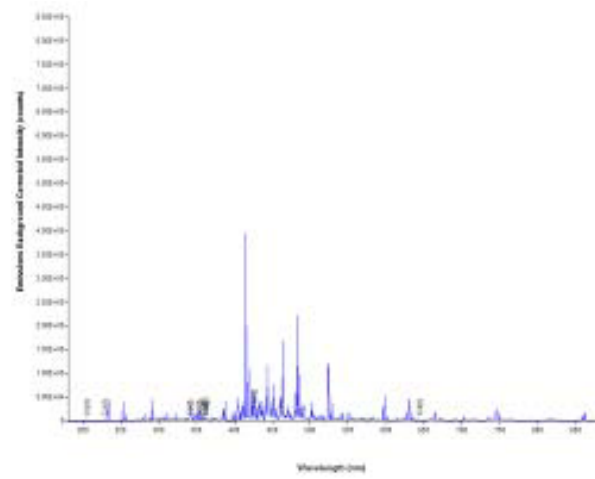


Figure 8-4. A broadband view of the ABF-LIPS spectrum at point 4.

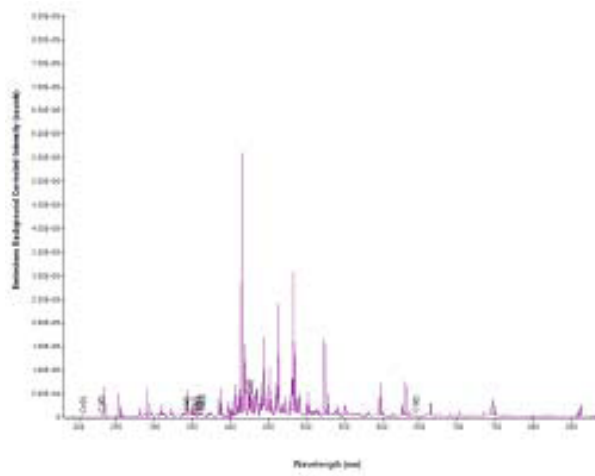


Figure 8-5. A broadband view of the ABF-LIPS spectrum at point 5.

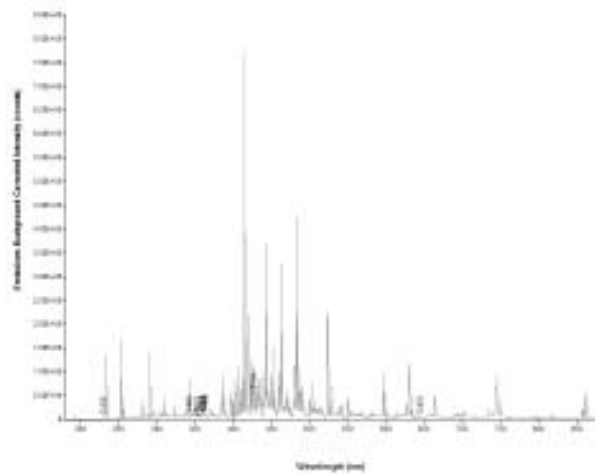


Figure 8-6. A broadband view of the ABF-LIPS spectrum at point 6.

Chromium species were identified within the window of 420-430 nm using the triplet of 425, 427, and 429. The results presented in Figures 9-1 through 9-6 are baseline-corrected. The peak height of wavelength 425nm was used for quantitative analysis (configuration [3d5(6s)4s-3d]). The flow skewness problem discussed earlier can be seen in Figures 9-1 through 9-6.

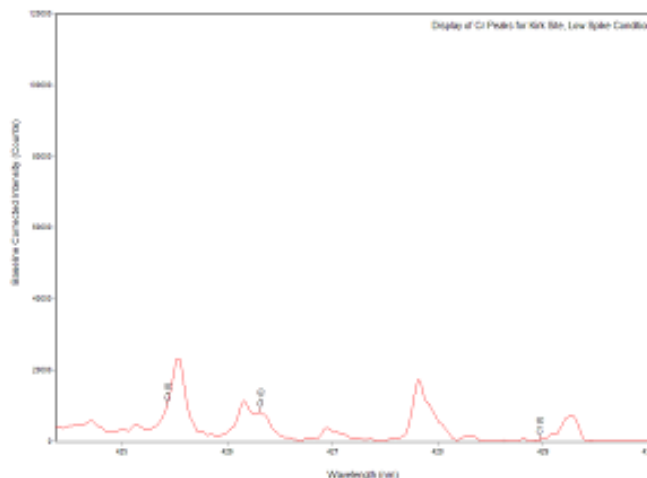


Figure 9-1. A focused view of the background corrected ABF-LIPS Cr spectrum at point 1.
Notice the Cr wavelength triplet at 425, 427, and 429.

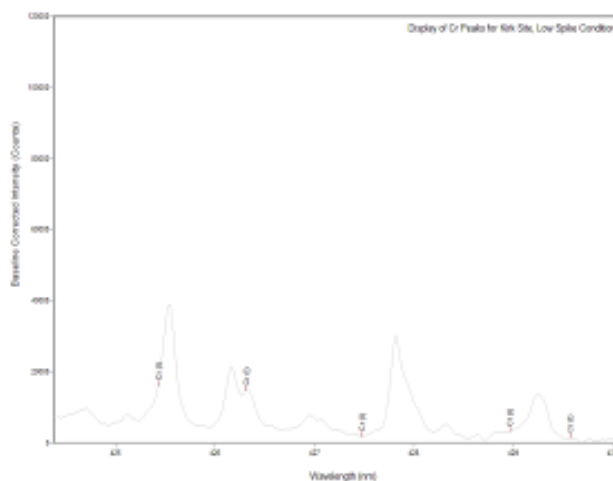


Figure 9-2. A focused view of the background corrected ABF-LIPS Cr spectrum at point 2.
Notice the Cr wavelength triplet at 425, 427, and 429.

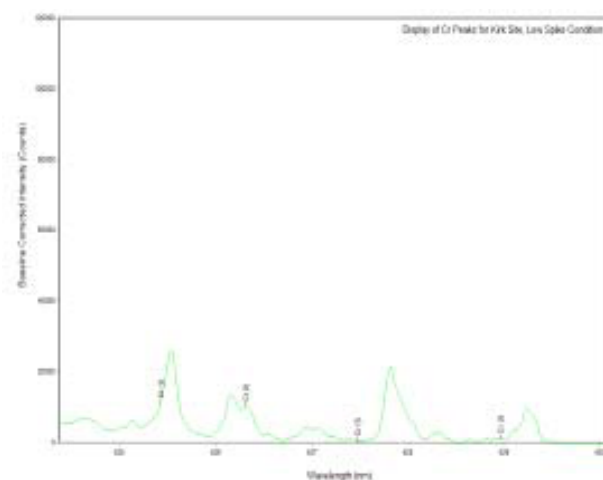


Figure 9-3. A focused view of the background corrected ABE-LIPS Cr spectrum at point 3.
Notice the Cr wavelength triplet at 425, 427, and 429.

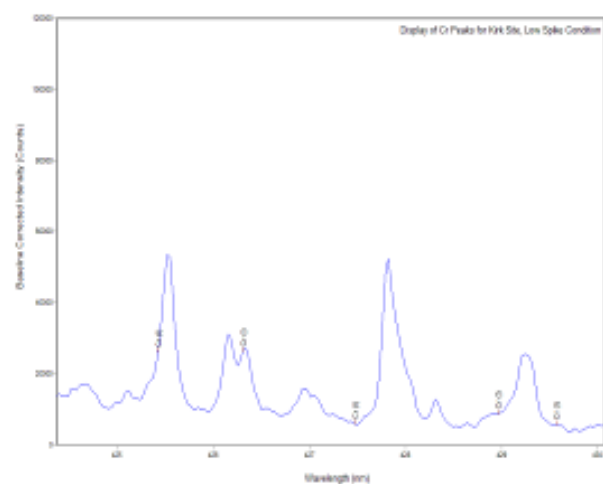


Figure 9-4. A focused view of the background corrected ABE-LIPS Cr spectrum at point 4.
Notice the Cr wavelength triplet at 425, 427, and 429.

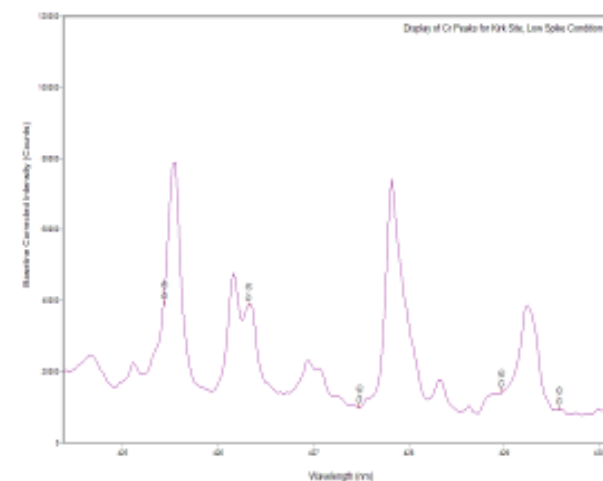


Figure 9-5. A focused view of the background corrected ABE-LIPS Cr spectrum at point 5.
Notice the Cr wavelength triplet at 425, 427, and 429.

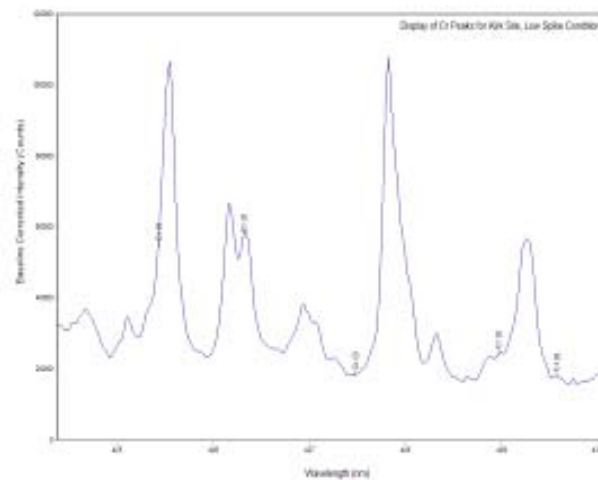


Figure 9-6. A focused view of the background corrected ABF-LIPS Cr spectrum at point 6.
Notice the Cr wavelength triplet at 425, 427, and 429.

The results for nickel are shown in Figures 10-1 through 10-6. Again, these results consistently indicate that the flow was skewed toward the duct wall at the locations 5 and 6. The wavelength used to quantify Ni content was 351.06nm [3d9(2D)4s)-3d].

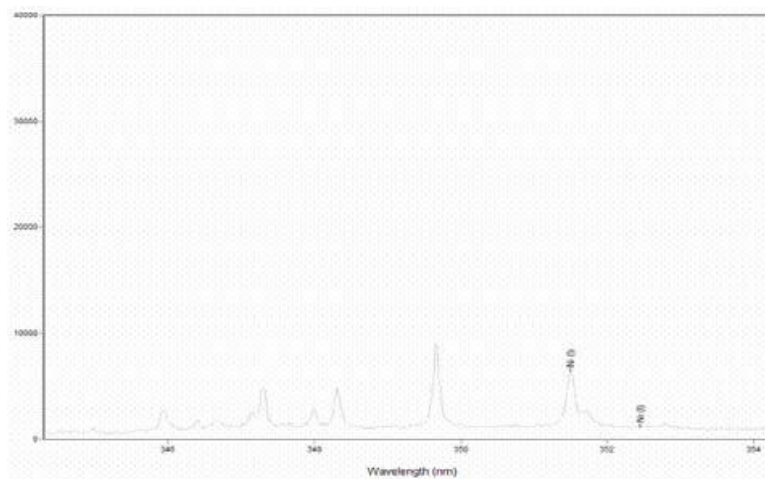


Figure 10-1. A focused view of the background corrected ABF-LIPS Ni spectrum at point 1.

Figure 10-2. A focused view of the background corrected ABF-LIPS Ni spectrum at point 2.

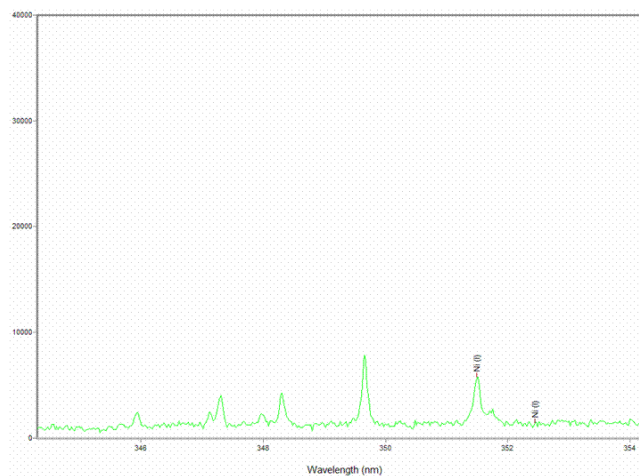


Figure 10-3. A focused view of the background corrected ABF-LIPS Ni spectrum at point 3.

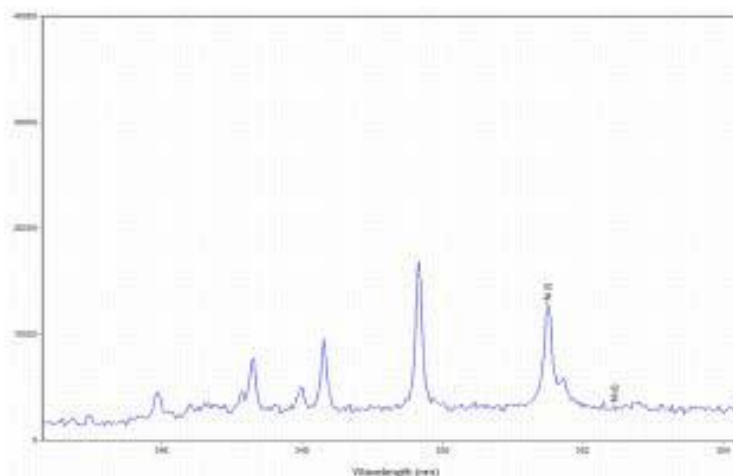


Figure 10-4. A focused view of the background corrected ABF-LIPS Ni spectrum at point 4.

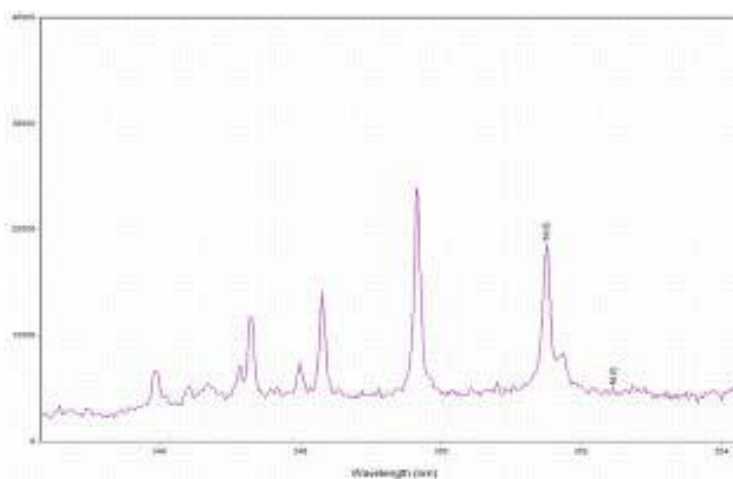


Figure 10-5. A focused view of the background corrected ABF-LIPS Ni spectrum at point 5.

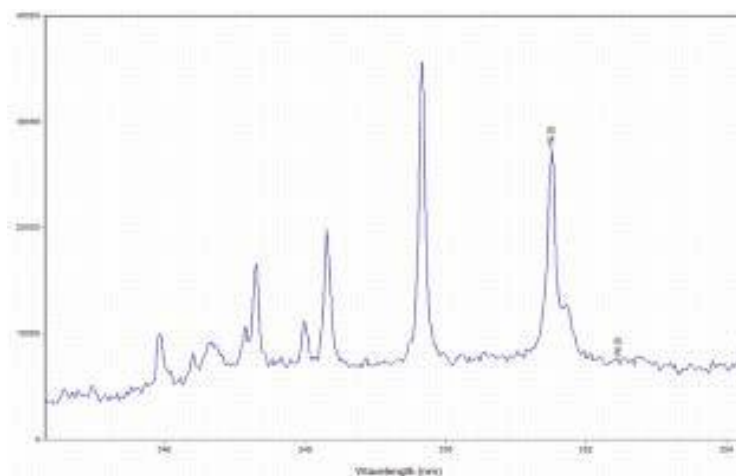


Figure 10-6. A focused view of the background corrected ABE-LIPS Ni spectrum at point 6.

The results for cadmium are shown in Figures 11-1 through 11-6. These results also indicate that the flow was skewed toward the wall at locations 5 and 6. The wavelengths used to quantify Cd were 537.8 and 734.65 nm.

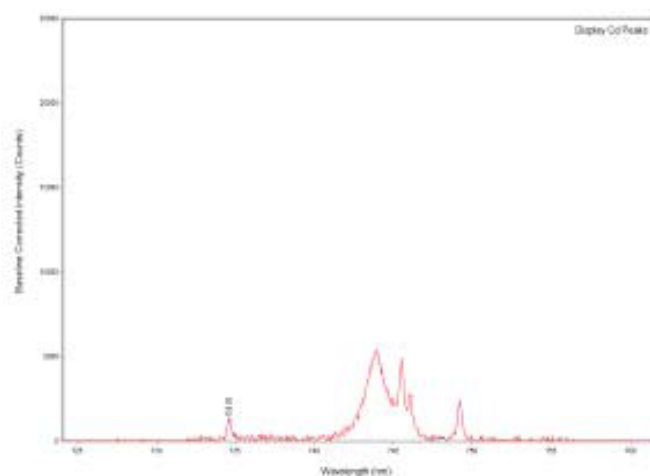


Figure 11-1. A focused view of the baseline corrected ABE-LIPS Cd spectrum at point 1.

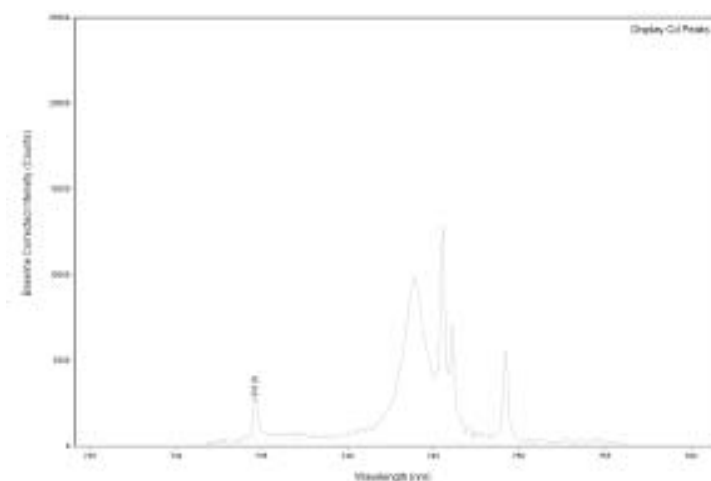


Figure 11-2. A focused view of the baseline corrected ABE-LIPS Cd spectrum at point 2.

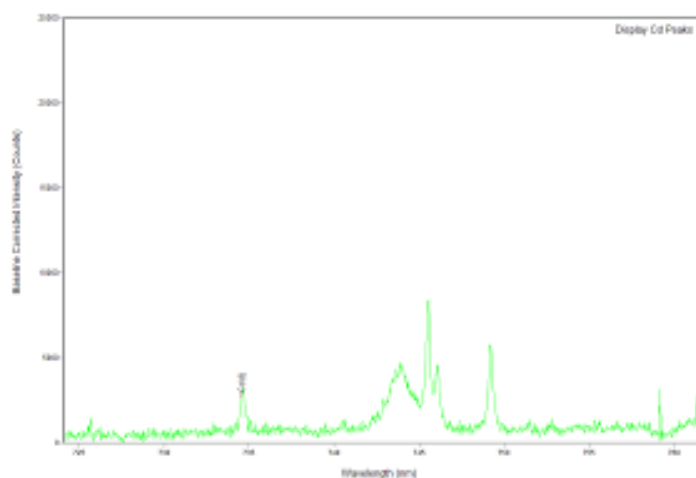


Figure 11-3. A focused view of the baseline corrected ABF-LIPS Cd spectrum at point 3.

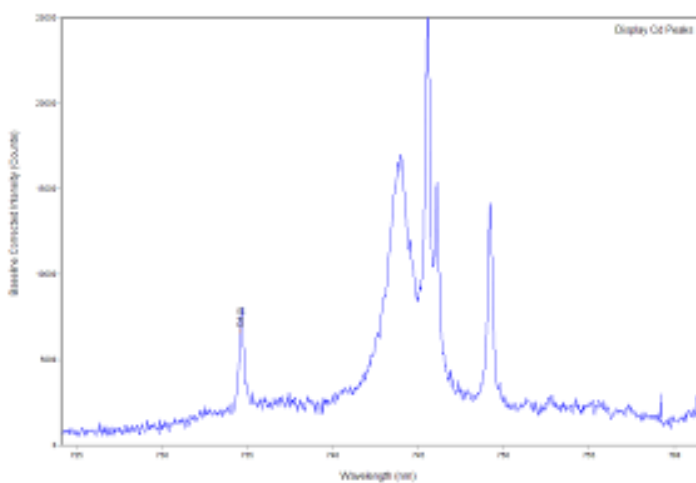


Figure 11-4. A focused view of the background corrected ABFLIPS Cd spectrum at point 4.

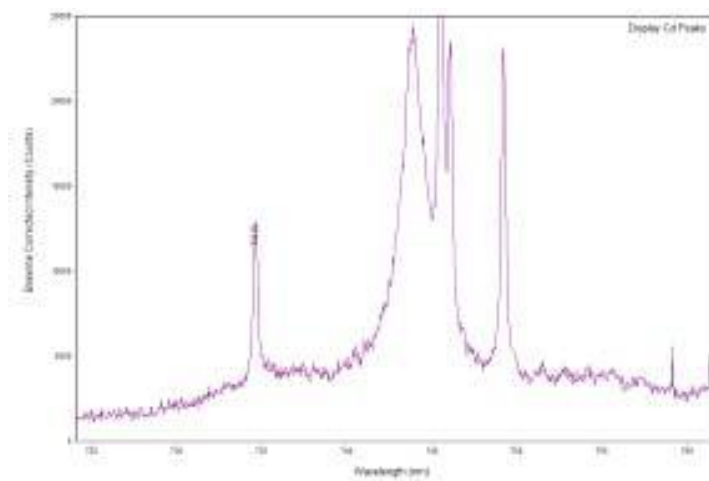


Figure 11-5. A focused view of the background corrected ABFLIPS Cd spectrum at point 5.

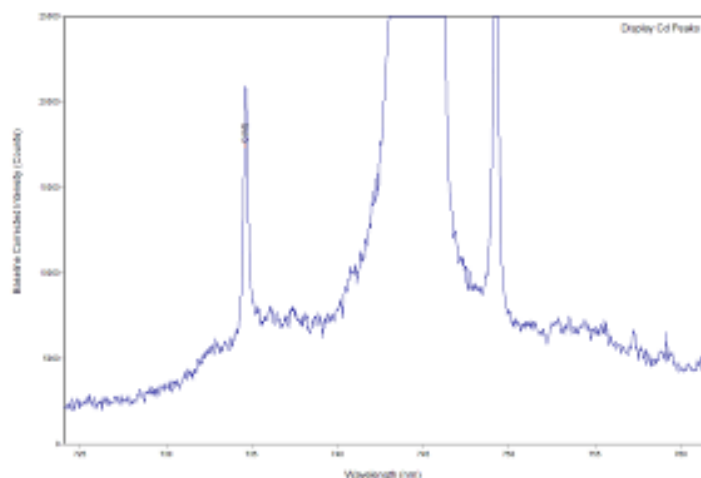


Figure 11-6. A focused view of the background corrected ABFLIPS Cd spectrum at point 6.

Medium Spike Condition – The Ni concentration in the median spiking solution was prepared to be 702 μ g/L, Cr 601 μ g/L, and Cd 601 μ g/L. Figures 12-1 through 12-6 show the broadband view of the ABF-LIPS spectra obtained under the medium spiking condition at the 6 probe locations. It is interesting to note that, based on these 6 plots, the velocity distribution across the duct at the Kirksite furnace appears to be more uniform than previously seen during the baseline and low spiking conditions. There were no significant differences in the peak heights of elements at various probe locations from one side to the other side of the duct wall during the medium spike runs.

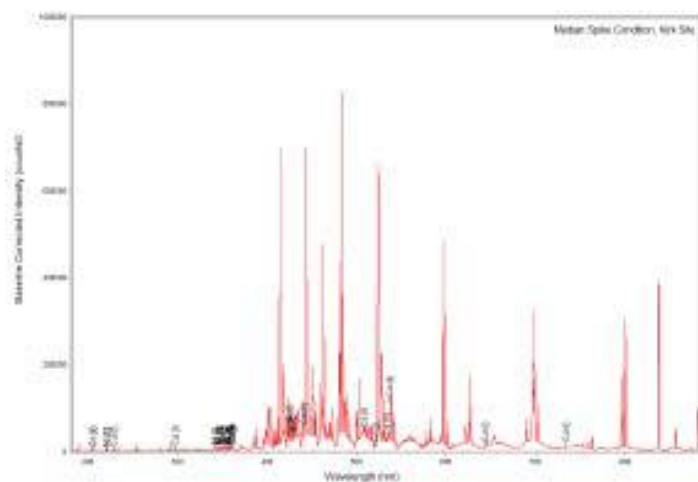


Figure 12-1. Broadband ABFLIPS spectrum for Kirksite emissions spiked with the median strength solution.

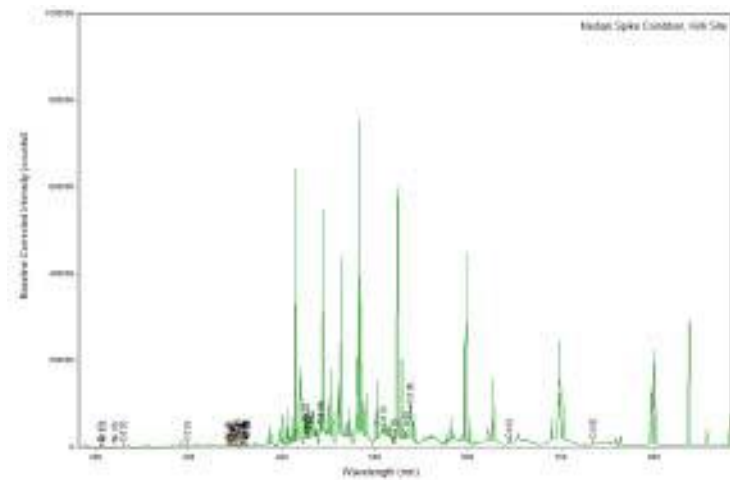


Figure 12-2. Broadband ABFLIPS spectrum for Kirksite emissions spiked with the median strength solution.

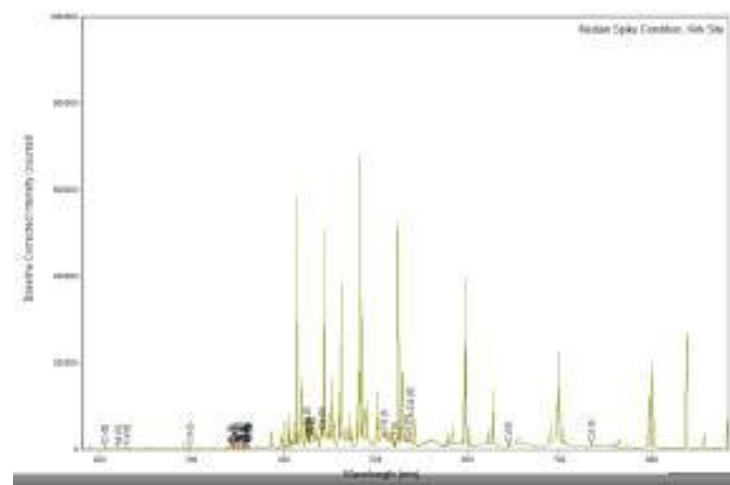


Figure 12-3. Broadband ABFLIPS spectrum for Kirksite emissions spiked with the median strength solution.

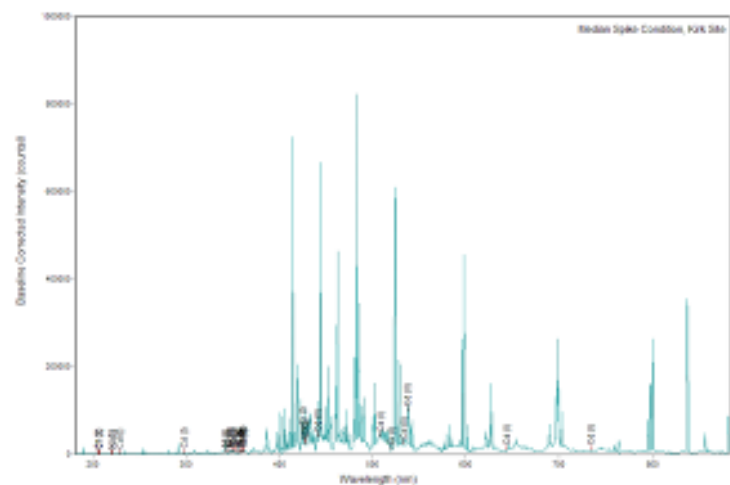


Figure 12-4. Broadband ABFLIPS spectrum for Kirksite emissions spiked with the median strength solution.

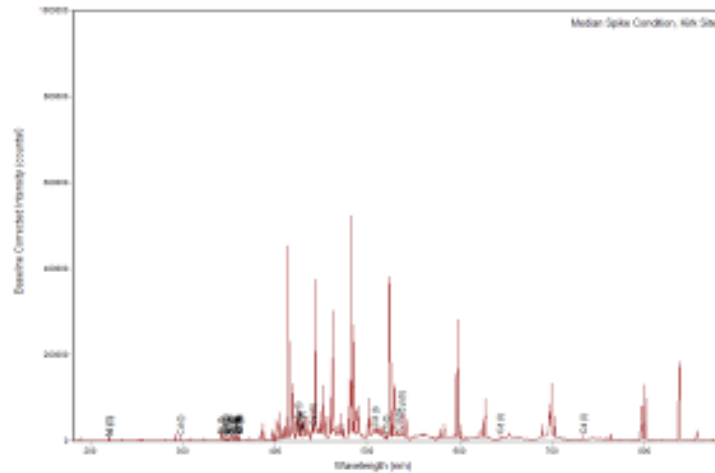


Figure 12-5. Broadband ABFLIPS spectrum for Kirksite emissions spiked with the median strength solution.

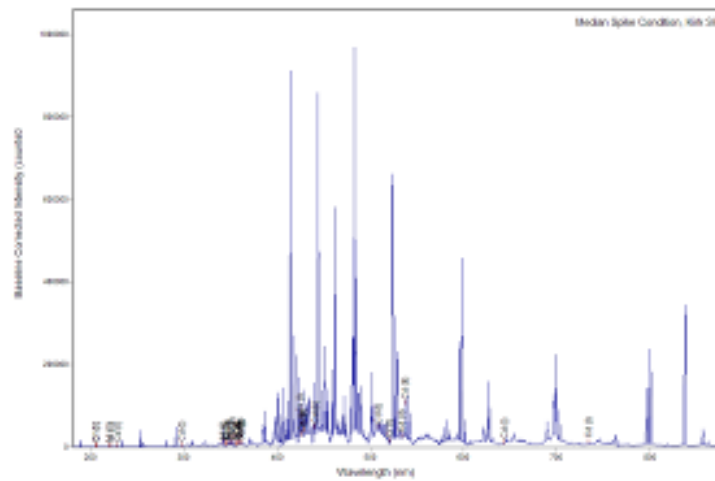


Figure 12-6. Broadband ABFLIPS spectrum for Kirksite emissions spiked with the median strength solution.

The nickel, chromium, and cadmium concentrations for spiked aerosols are determined from the peak-height readings at their characteristic wavelengths (351.5nm for Ni, 425.5nm for Cr, and 537.8nm for Cd). Table 1 shows the baseline corrected peak-height readings at the three wavelengths for the 6 probe locations taken at the Kirksite under the median spiking condition.

Table 1. Summary data for the target elements at the Kirksite.

Low Spike Solution	330 $\mu\text{g}/\text{m}^3$	150	153
Median Spike	702	601	601
High Spike	2,727	6,000	6,003
Location	Ni, 351.5 nm	Cr, 425.5 nm	Cd, 537.8/734.7 ¹ nm
L*-1	3,578	23,146	1,305
L-2	6,364	38,185	3,071
L-3	5,782	25,887	3,183
L-4	12,680	51,750	8,030
L-5	18,540	78,795	12,993
L-6	27,400	106,643	20,828
6-point average (μ)	12,391	54,068	8,235
6-point std. dev. (σ)	9,174	32,813	7,503
COV ($=\sigma/\mu$) in %	74%	60.7%	91.1%
M*-1	11,002	102,672	11,395
M-2	9,828	86,178	8,955
M-3	8,670	78,304	8,293
M-4	11,574	97,236	9,518
M-5	7,649	53,044	5,225
M-6	17,929	103,164	9,378
6-point average (μ)	11,109	86,766	8,794
6-point std. dev. (σ)	3,642	19,187	2,032
COV ($=\sigma/\mu$) in %	32.8%	22.1%	23.1%
H*-1	548	96	-285
H-2	971	1,323	-36
H-3	3,767	5,446	4,090
H-4	2,239	1,343	5,068
H-5	2,394	931	9,009
H-6	1,291	---	9,592
6-point average (μ)	1,868	1,828	6,940
6-point std. dev. (σ)	1,175	2,085	2,765
COV ($=\sigma/\mu$) in %	62.9%	114.1%	39.8%

Note:

(i) X* indicates the spiking condition. L=low; M=median; H=high.

(ii) 734.71-nm wavelength was used for low-spiking condition, while 537.8 nm was used for both median and high spiking conditions.

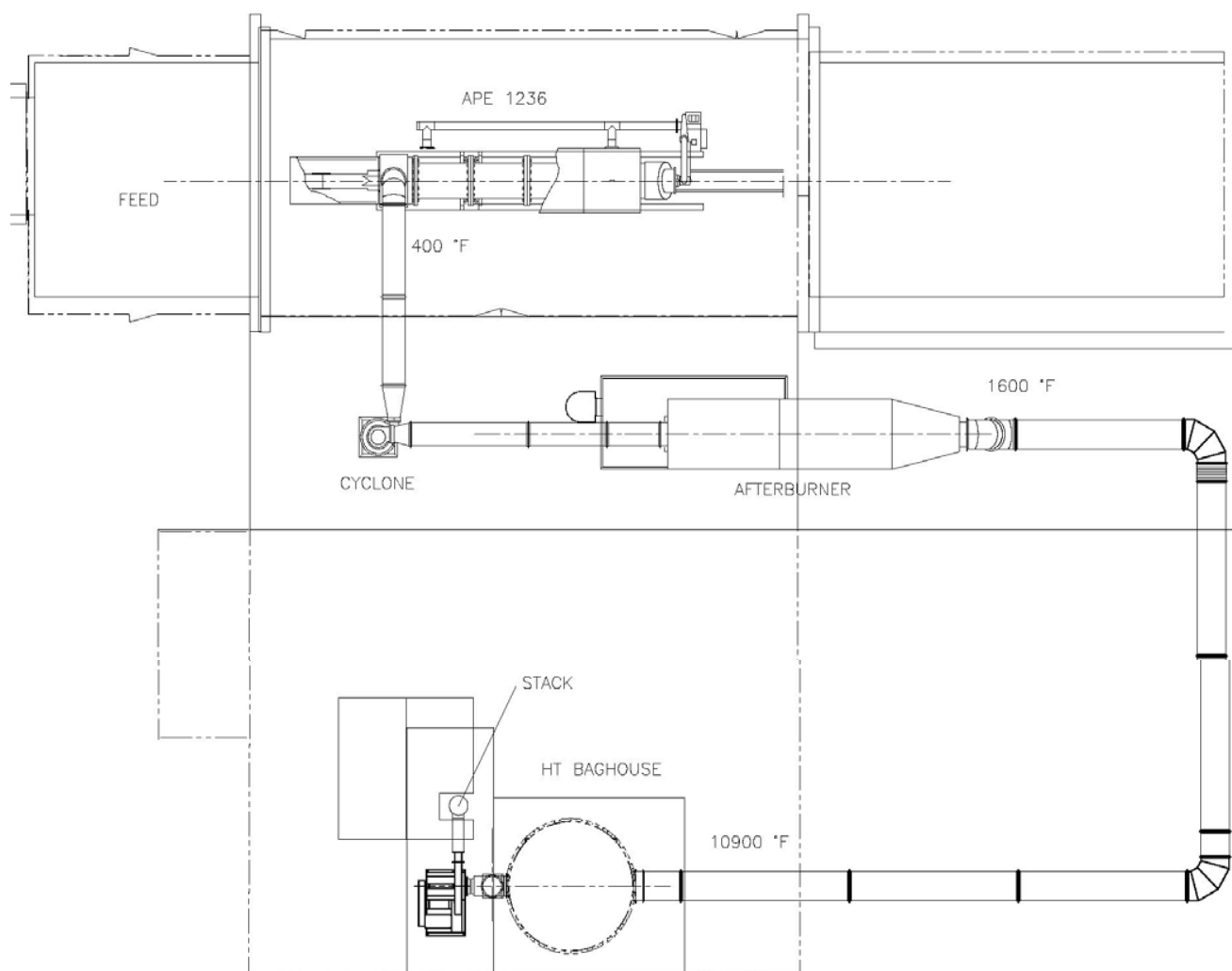
The results show that the spiked metal concentrations were statistically identical between the low and the median spike conditions. Further, the average concentrations obtained for the three metals under the high spike condition were lower than those obtained under the low- and the medium-spiked conditions. This finding is consistent for all three elements and suggests that either the metals spiking failed or that the ABF-LIPS readings were in error. The results of the RM testing suggest that the ABF-LIPS readings are in error at the Kirksite furnace.

To examine the spatial variation irrespective of the performance of aerosol spiking, the coefficient of variation (COV) is calculated as the ratio of the SD to the average. This COV value represents the overall variation across the duct measured by ABF-LIPS at the 6 probe locations. For example, in the low spiking experiment, there was 61% to 91% variation in aerosol metal contents observed across the emission duct at the Kirksite furnace. This is consistent with the duct flow distribution being skewed.

Interestingly, in the medium spiking condition, the COV values were between 22% and 33%, three times smaller than that found for the low-spike condition. The range of the COV values for the 3 metals in the medium-spiking case was also smaller than that in the low case raising a question about the ABF-LIPS detection and adequacy of the low spiking solution. In other words, it is possible that the metal contents produced by the low-spiking solution were insufficient for ABF-LIPS to distinguish it from the baseline; thus, this led to high cross-sectional variations in the observed metal contents. The flow itself might not be skewed. We will verify this further in the data from the other two sites in the following section.

This conclusion appears to be reinforced with the results from the high-spiking experiment where the COV values for the 3 metals ranging from 40% to 114%. The averaged peak heights for each of the 3 metals for the high-spiking case were lower than that for the median-spiking case, or even the low-spiking case.

APPENDIX E TEAD TEST FURNACE SCHEMATIC



Tooele Army Depot 1236M2 Munitions Deactivation Test Furnace schematic showing September 2005 metals spiking and ABF-LIPS sampling locations



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