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ESTCP COST AND PERFORMANCE REPORT: WP-0213

**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
AED	Ammunition Equipment Directorate
APCS	Air Pollution Control System
APE	Ammunition Peculiar Equipment
ATCM	Airborne Toxic Control Measure
BRAC	Base Realignment and Closure
BTU	British Thermal Unit
CAA	Clean Air Act
CAAA	Clean Air Act Amendments
CCD	Charge Coupled Device
CEMS	Continuous Emission Monitoring System
CFD	Computational Fluid Dynamic
CFR	Code of Federal Regulations
DF	Deactivation Furnace
DGRC	Defense Non-Tactical Generator and Rail Center
DL	Detection Limit, also Lower Detection Limit (LDL)
DoD	Department of Defense
EPA	Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
HAP	Hazardous Air Pollutant
HEPA	High Efficiency Particulate Air (filter)
ICCD	Intensified Charge Coupled Device
ICP	Inductively Coupled Plasma
ID	Inside Diameter
IOC	Industrial Operations Command
K	Thousands (of dollars)
LDL	Lower Detection Limit, also Detection Limit (DL)
MDL	Maximum Detection Limit
MS	Mass Spectroscopy
NADEP	Naval Aviation Depot
NAMMO	Nordic Ammunition Company
NDIR	Non-dispersive Infrared
NFESC	Naval Facilities Engineering Service Center
NESHAP	National Emission Standards for Hazardous Air Pollutants
NPV	Net Present Value
O&M	Operations and Maintenance
ORNL	Oak Ridge National Laboratory
OSHA	Occupational Safety and Health Administration
PB	Parson Brinckerhoff
PLC	Programmable Logic Controller
ppm	Parts Per Million
RA	Relative Accuracy
RDA	Redevelopment Agency
RM	Reference Method

RV	Reference Value
SCFM	Standard Cubic Feet Per Minute
SERDP	Strategic Environmental Research and Development Program
SMPA	Scanning Mobility Particle Analyzer
TACOM	Army Tank-automotive and Armaments Command
TEAD	Tooele Army Depot
TRI	Toxic Release Inventory
VOC	Volatile Organic Compound
WFRMS	Waste Feed Rate Monitoring System
XRF	X-ray Fluorescence (spectroscopy)

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EXECUTIVE SUMMARY

Background

This report describes field testing of a novel continuous emissions metals analyzer, the Aerosol Beam-Focused Laser Spectrometer (ABF-LIPS), developed by Oak Ridge National Laboratory 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 (HAPs) 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 hazardous air pollutants (HAPs). Continuous emission monitoring systems (CEMS) provide an effective means for monitoring the level of hazardous air pollutants (HAPs) in real-time and ensures that the maximum achievable control technology is performing as specified.

The principle of operation of ABF-LIPS is a pulsed laser beam is 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 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 (ABF) capability improves the detection and sensitivity of traditional LIPS by aerodynamically focusing aerosol particles to a point, increasing the local aerosol concentration which significantly improves 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.

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 (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), and the results between ABF-LIPS and the reference method were compared.

The primary performance criteria for the tests was the relative accuracy (RA), or the agreement (bias) of the results reported by ABF-LIPS with the result obtained by standard EPA 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 reference method 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). The reference method, 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.

Regulatory Drivers

In 1990, Congress amended Section 112 of the Clean Air Act (CAA) requiring the EPA to identify and regulate all significant stationary sources that emit any of 189 HAPs. Currently, the EPA 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 EPA is developing regulations to limit emissions of the HAP metals from sources such as incinerators and coal-fired power plants, among others. The 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 the EPA (EPA/625/R-97/001, 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 of the EPA 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 EPA approved methods. Further development of ABF-LIPS will be required, however, prior to additional validation testing and eventual regulatory acceptance.

Demonstration Results and Implications

The first test was conducted at the Naval Aviation Depot (NADEP) North Island in San Diego, California during June 2003. A chromium plating bath exhaust, a nickel plating bath exhaust, and a molten metal (Kirksite) furnace were sampled. The second demonstration test was conducted at Tooele Army Depot (TEAD) in Tooele, Utah using the Ammunition Equipment Directorate's (AED's) Ammunition Peculiar Equipment (APE) 1236M2 test furnace, a munitions deactivation test incinerator. Each source was spiked with an aerosol of three to five test metals (cadmium, chromium, lead, mercury, nickel) at each of three concentrations (low, medium, and high). Each concentration was run in quadruplicate, resulting in a total of twelve runs for each source. The acceptance level for RA is 20% per PS-10 (EPA's Performance Specification 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 chromium and nickel 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 (cadmium, chromium, and nickel). Pearson correlation coefficients ranged from negative (anti-correlated), to weakly positive (i.e. random). In contrast, the reference method 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 Tooele Army Depot (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 reference method 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 reference method 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 cadmium or chromium was detected, and nickel was 145% lower and lead 1000% lower than the reference method results. Mercury was within 5% at the low concentration.

The TEAD reference method data are suspect, however. 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 reference method data is inherently flawed, and comparisons to the ABF-LIPS results are therefore likely unreliable.

While PS-10 validation of ABF-LIPS did not meet the relative accuracy 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 six minutes).

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, however, 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.

End-user Issues

The major components of ABF-LIPS are commercially available instruments, including a high-power 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 \$160K, and annual operation & maintenance (O&M) costs are projected to be \$10K. Assuming the useable life of an ABF-LIPS unit is 10 years, the annualized cost is \$26K (annual O&M + \$160K/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 \$14K/year per source. Savings would be multiplicative

at facilities where a single ABF-LIPS unit could be used portably on multiple sources. Such is the case at many DoD installations. In addition, it is the only method that will provide continuous emission monitoring, an expected requirement of upcoming regulations.

1 TECHNOLOGY DESCRIPTION

1.1 Introduction

Continuous emission monitoring systems (CEMS) provide an effective means for monitoring the level of hazardous air pollutants (HAPs) in real-time. A CEM also ensures that the maximum achievable control technology is performing as specified. HAPs include the following metals: arsenic, antimony, barium, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, nickel, selenium, silver, and thallium. 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 and/or burning, and waste combustion. All of these activities are important to the missions of the Department of Defense (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 one-hour period for medium to high concentration levels, and a two-hour 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 and/or engineering process control.

Facilities that do not have a CEM 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 XCEM 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 (CAA) requiring the EPA to identify and regulate all significant stationary sources that emit any of 189 HAPs. Currently, the EPA 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 EPA is developing regulations to limit emissions of the HAP metals from sources such as incinerators and coal-fired power plants, among others. The proposed limits for hazardous waste incinerators for metals are shown in Table 1-1. The 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 the EPA (EPA/625/R-97/001, 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 of the EPA 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 EPA 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.

Carcinogenic Metals	µg/m³ (annual limit)	Non-Carcinogenic Metals	µg/m³ (annual limit)
Arsenic	2.3×10^{-3}	Antimony	0.3
Beryllium	4.1×10^{-3}	Barium	50
Cadmium	5.5×10^{-3}	Lead	0.09
Chromium	8.3×10^{-4}	Mercury	0.3
		Silver	3
		Thallium	0.3

Table 1-1. Proposed EPA Hazardous Waste Incineration Standards, Tier III Reference Air Concentrations. (40 CFR Parts 260, 261, 264 and 270, Federal Register Volume 55, No. 82, April 27, 1990)

1.2 Technology Development and Application

Measurement of metal HAPs using laser-induced plasma spectrometry (LIPS) has been adapted to a field portable instrument, ABF-LIPS. The aerosol beam focusing (ABF) capability improves the detection and sensitivity of traditional LIPS by aerodynamically focusing aerosol particles to a point, increasing the local aerosol concentration which significantly improves the signal-to-noise ratio. The principle of operation of ABF-LIPS is a pulsed laser beam is 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 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 Oak Ridge National Laboratory with funding from the Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP).

ABF-LIPS was developed under the Strategic Environmental Research and Development Program (SERDP) during FY97-FY00. ABF-LIPS addresses a number of the shortcomings associated with traditional stack monitoring and commercially available metals CEMs. ABF-LIPS, because of its portability, can be mounted at an emission source and requires no long sampling line, which virtually eliminates sample loss. The present instrument design comprises

physical dimensions of 24"(L) x 24" (W) x 24" (H) and a weight of about 50 lbs. Unlike the Trace AIR metals CEM, 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 two minutes.

1.3 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) that 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 also be used in area detection, for instance to measure beryllium aerosol in a nuclear manufacturing facility (Cheng et al., 2004; Cheng and Smithwick, 2004).

The ABF-LIPS technique improves the detection and sensitivity of traditional LIPS (also known as LIBS – Laser Induced Breakdown Spectroscopy) by aerodynamically focusing aerosol particles to a point, increasing the local aerosol concentration which significantly improves 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 CEM (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 US Patent No. 6,359,687. A schematic of ABF-LIPS is provided in Figure 1-1. Figures 1-2 and 1-3 illustrate the principles of aerosol focusing and concentration of particles.

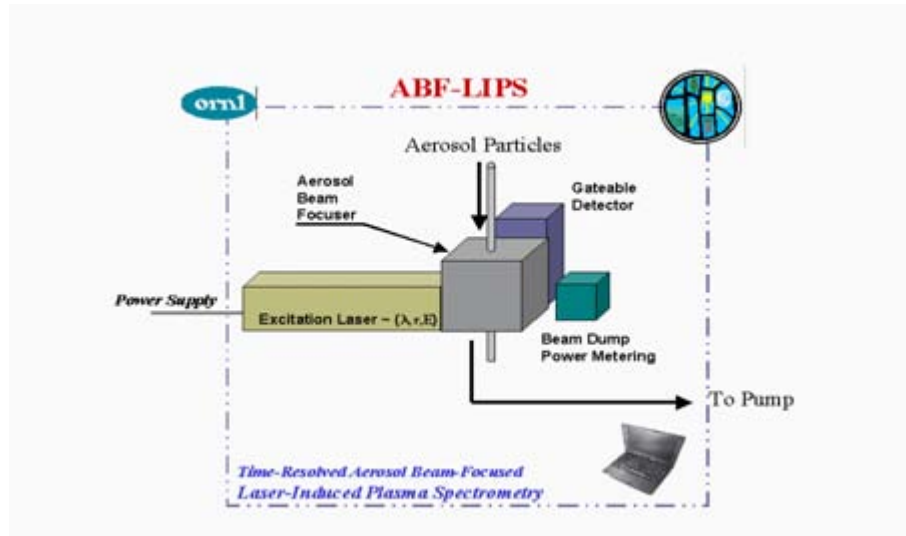


Figure 1-1. Schematic of the Aerosol Beam Focused Laser Induced Plasma Spectrometer (ABF-LIPS).

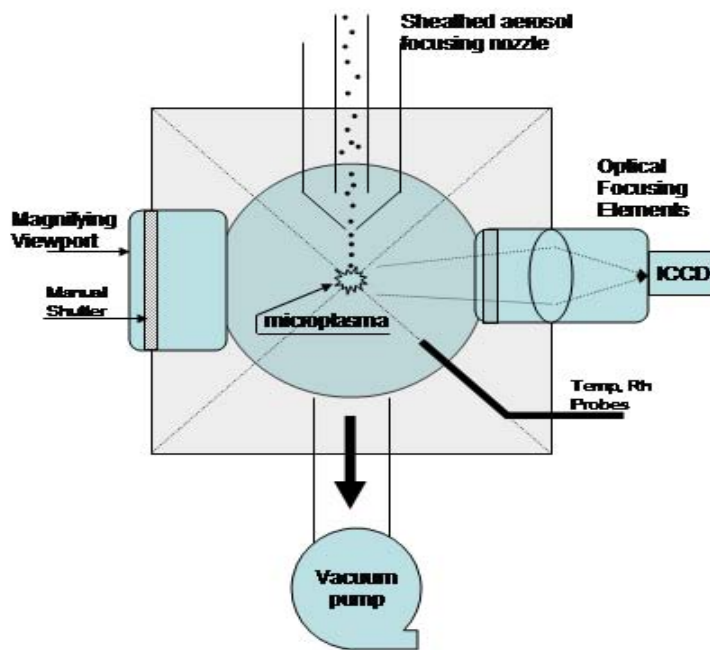


Figure 1-2. Schematic of Aerosol Focusing Process.

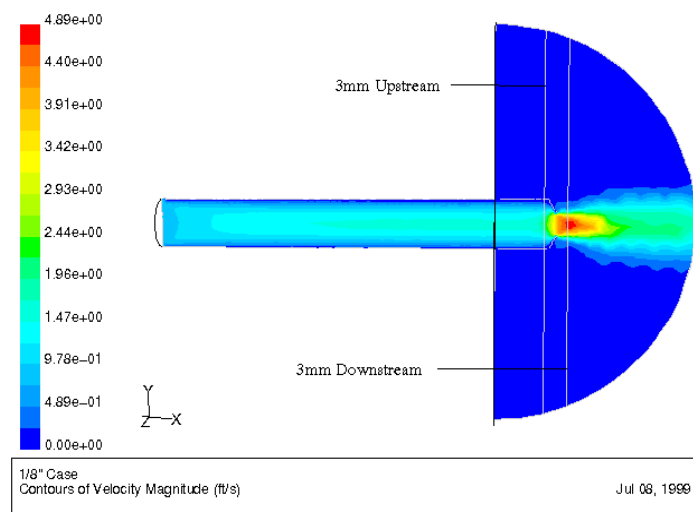


Figure 1-3. Focusing Simulation by Computational Fluid Dynamic (CFD) Modeling.

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 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 samples 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.

Performance Specification-10 (PS-10) for CEMS require that relative accuracy be within 20% of the mean of the reference method. Instrument drift from the calibration standard and the zero value must not exceed 5% (values measured daily over 7 days) per PS-10.

ABF-LIPS is a relatively simple instrument to operate; the latter field test at Tooele Army Depot required setup of about 1 hour 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. Thanks to the portability of the unit, advanced trouble-shooting could be performed by economically shipping the unit to the factory or repair facility.

1.4 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 lead, chromium, nickel, mercury, zinc, copper, carbon, iron, aluminum, and sulfur. 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 that also served as an aerosol sampling manifold.

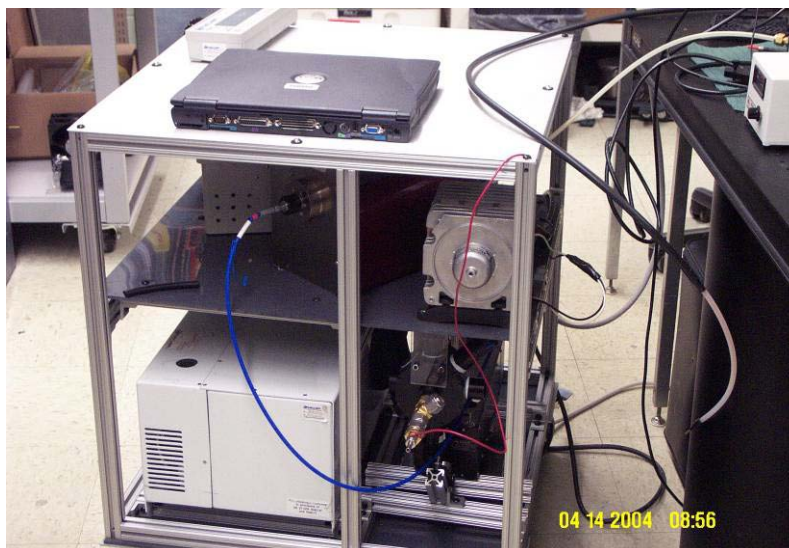


Figure 1-4. ABF-LIPS prototype.

The technology was further developed and subsequently refined in 2000. A field-portable unit, shown in Figure 1-4, 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.

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 Oak Ridge National Laboratory (ORNL) in Knoxville, Tennessee, and a chemical disrupter located at the Eastman Chemical Company in Kingsport, Tennessee (Cheng and Vannice, 2003; Cheng, 2003). These sources included a diesel engine research facility where chromium, vanadium, copper, and platinum were of interest, and an industrial waste incinerator at the Eastman Chemical Company in Kingsport, Tennessee. 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 chromium, mercury, and beryllium. The Eastman test results were presented at the Air and Waste Management Association national meeting in San Diego, CA, in June 2003. Cheng (2003) detailed the test results from the Eastman campaign in 2002.

1.5 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 six minutes) 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 1-1 provides a summary comparison of ABF-LIPS with other commercial and known instruments that measure metal emissions. With the exception of the TraceAir and XCEM, 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 XCEM (Cooper Environmental, Inc.) is much smaller than the TraceAir but is not portable. The XCEM has a minimum detection limit of 1 to 3 ug/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 ug/dscm and below. Maximum detection limits (MDL) for the ABF-LIPS technique could be increased by lowering the gain of the detector. This would virtually unlimit the 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 XCEM and ABF-LIPS use different detectors, they are more or less sensitive to various matrix interferences, and so one system may be more suitable for a particular application than the other.

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 Spectrograph	Yes	No	No	No	No	No	No	
	Echelle	Echelle		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 (HxWxD)	24"x 18" x 9", 45 lbs	Trailer	24"x36"x48", 400 lbs	15"x29"x12", 132 lbs	19"x19"x13.8", weight unknown	16"x20"x28.3", 43 lbs	On a wheeled platform	72"x36"x36"
Cost	\$90-\$150,000		\$275,000		~ \$60,000			~\$250,000

Table 1-2. Comparison of ABF-LIPS with Other Metals Emission Monitors.

2 DEMONSTRATION DESIGN

The objectives of this Environmental Strategic Technology Certification Program (ESTCP) project are to:

- Field-validate ABF-LIPS performance by collecting data under real-world conditions and comparing the data to data obtained simultaneously by an EPA-certified standard reference method. The performance parameters include:
 - Relative Accuracy (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/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.

2.1 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: relative accuracy (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 2-1 further describes the performance criteria, acceptance criteria requirements, procedures/action and notes.

QA Indicator	Description	Requirement	Action	Notes
Relative Accuracy (bias)	Result compared to reference method	+/-20%	9 data pairs minimum at 3 levels	12 data pairs at 3 levels will be collected
2 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 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 minutes	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) 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.
Practical Limit of Quantitation	Minimum detection level in this application	10X the Standard Deviation at the blank level	Measure zero or ambient air and calculate SD of mean	ABF LIPS ambient air produced no photon counts

Table 2-1. Data Quality and Quality Assurance Objectives.

EPA Performance Specification 10 (PS-10, Appendix A) is a draft proposal specification for assessing the acceptability of a multi-metal CEM in terms of quality assurance objectives. As of the publication date of this report, PS-10 is still in its proposed draft form as originally proposed in 1996. 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:

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

Obtain a minimum of three pairs of CEM and RM measurements for each metal required and at each level required (see Section 7.1 of PS-10, included as Appendix A). 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:

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

where $\bar{d}$ is equal to the arithmetic mean of the difference d , of the paired CEMS and RM data set, SD is the standard deviation 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 twelve test runs included four test runs at each of three spiked metals concentrations (low, medium, and high concentration). The metals included cadmium, chromium, and nickel for the field test at NADEP. Lead and mercury were added as for the field test at the munitions deactivation furnace at Tooele Army Depot.
- Calibration Drift. The CEM design must allow the determination of calibration drift at concentration levels commensurate with the applicable emission standard for each metal monitored. The CEM calibration may not drift or deviate from the reference value (RV) of the calibration standard used for each metal by more than 5 percent of the emission standard for each metal. The calibration shall be performed at a point equal to 80 to 120 percent of the applicable emission standard for each metal.
- Zero Drift. The CEM design must allow the determination of calibration drift at the zero level (zero drift) for each metal. If this is not possible or practicable, the design must allow the zero drift determination to be made at a low level value (zero to 20 percent of the emission limit value). The CEM zero point for each metal shall not drift by more than 5 percent of the emission standard for that metal. The prescribed period is once each day for 7 consecutive days.

2.2 Selection of Test Facilities

Two facilities were selected for demonstration testing. The first test was conducted at the Naval Aviation Depot (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 Tooele Army Depot (TEAD) in Tooele, Utah using the Ammunition Equipment Directorate's (AED'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 Tooele during October 2004 was aborted due to freezing weather and blowing snow. The second field test at Tooele was completed during September 2005. The test facilities for NADEP and TEAD are further described in the following subsections.

2.2.1 Test Facility Selection – NADEP (Naval Aviation Depot North Island)

Naval Air Depot, North Island has over 80 years of service to the fleet. The Depot 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 total Navy and other agencies of the Department of Defense 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 cadmium, chrome, and nickel lines. Chromium coatings provide excellent wear resistance and corrosion protection. Hard chrome coatings are thick layers of chromium used to give a part extra wear resistance. Nickel coatings are used to improve corrosion resistance, wear resistance, and magnetic characteristics. Nickel is considered to be very flexible in metal plating because the properties of nickel coatings can be controlled and varied relatively easily.

The low temperature demonstration test was conducted at a plating facility at NADEP June 15-18, 2003. Two plating bath sources were tested: a hard chrome plating line and an electroless nickel 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 nickel and chrome plating line were located following the emission control devices; the Kirksite furnace sampling location was prior to emission control devices. The Kirksite furnace has no emissions control device.

2.2.1.1 Chrome Plating

The Naval Aviation Depot conducts metal finishing operations that utilize five hard chrome plating tanks located in Building 472. The facility typically plates 3-5 million amp-hours per year and is identified as a Small Hard Chromium 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 2-1. 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-inch diameter horizontal duct before entering a 100-HP blower and exiting to the atmosphere via a stack.

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. 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 washdown 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 minutes for 30 seconds) 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 2-2. The exhaust stack diameter is 49.5 inches. Two existing test ports at right angles accommodate dual train reference method (EPA Method 29) probes; a third test port was installed (several inches 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 concentration).



Figure 2-1. Chromium plating bath operation at NADEP.



Figure 2-2. Sampling port on chromium plating bath exhaust on roof of building at NADEP.

2.2.1.2 Electroless Nickel

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

The electroless nickel 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 nickel 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 2-3). The source tests on the nickel 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 2-3. Electroless nickel plating bath exhaust stack on roof of building at NADEP.

2.2.1.3 Kirksite Furnace

The Naval Aviation Depot conducts casting operations in Building 65 that utilizes a furnace for the melting of a zinc-base alloy known as Kirksite. Kirksite is a moderate strength zinc-base alloy that was 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, 800-850F. 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 atmosphere. A photograph of the Kirksite melting pot and hood are included as Figure 2-4.

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.



Figure 2-4. Kirksite furnace melting pot in hood at NADEP.

2.2.2 Test Facility Selection – TEAD (Tooele Army Depot)

Tooele Army Depot (TEAD) is a Tier 1 active joint ammunition storage site on 23,610 acres one hour west of Salt Lake City, Utah. Tooele is responsible for shipping, storing, receiving, inspecting, demilitarization, and maintaining training and war reserve conventional ammunition and ammunition peculiar equipment (APE). TEAD has a test facility that includes a prototype APE 1236M2 deactivation furnace (DF), flashing furnace, and a number of structures where certain APE are developed, tested, and/or 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 deactivation furnace 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 2-5, consists of a main control panel, a conveyor feed/discharge system, a rotary furnace, a cyclone separator, an afterburner, continuous emissions monitors (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 2-5. APE 1232M2 Prototype Munitions Deactivation Furnace Demonstration Site, Tooele Army Depot, 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 (CEM) System

The CEM system measures CO and O₂ in the exhaust stack. The CEM sampling system 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 CEM system includes automatic calibration, which allows the monitors to be calibrated periodically with operation intervention. The CO monitor is a non-dispersive infrared (NDIR) analyzer with 0-200 parts per million (ppm) and 0-3,000 ppm dual range capability. The output from the CO monitor is corrected to 7% O₂ using data from the O₂ CEM.

Waste Feed Rate Monitoring System (WFRMS)

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 for the item being acceptable, 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 seconds.

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 ft long, 30.5-inch diameter retort toward the burner end by spiral flights. As the ammunition approaches the flame, they either detonate or burn 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 unit (BTU)/hr and a nominal turndown ratio of 4:1. The feed end temperature of the furnace ranges between 350-450 °F while the discharge end ranges from 800-1100 °F during normal operation. The rotary furnace is operated under a slight negative pressure and was operated at 1.4 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 90-95% removal a 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 that 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 from the kiln. This elevated temperature, and the added residence time, enhances the completeness of combustion of the explosives. The afterburner is capable of heating 4,000 standard cubic feet per minute (scfm) of flue gas from 350-450 °F to 1400-1600 °F with a minimum flues gas residence time of 2 seconds. 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 ration 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 lead 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-inch 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 that are 10 ft by 5.75 inches in diameter. This results in a total filter area of 2,330 square ft with a filtration velocity of 4.97 ft/s. The bag house operates with a delta pressure range of 0.5 to 6.0 inches 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 (APCS) by an induced draft

fan. The fan is capable of pulling 6,700 scfm at a draft (negative pressure) of 30 inches of water column.

Exhaust Stack

The A36 carbon steel, circular exhaust stack is approximately 30 ft high (34 ft with extension) and has a nominal inside diameter (ID) of 19.625 inches. A photograph of the exhaust stack is included as Figure 2-6.



Figure 2-6. APE 1236M2 Furnace Stack, Tooele Army Depot, Tooele, Utah.

2.2.2.1 Sampling Locations

The DF exhausts to a 19.625-in ID stack. Two 3 ¼ inch ID ports, located at right angles to each other, are 102 inches (5.2 duct-diameters) downstream and 86 inches (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 deg. F.

2.3 Physical Set-Up and Operation

2.3.1 North Island Aviation Depot

Three sources were tested at the North Island Aviation Depot (NADEP) in San Diego: a chrome plating bath, an electrode-free nickel 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.

2.3.1.1 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 reference method 29 sampling trains were set up on the roof of the building. Monitoring ports installed at right angles were already in place for reference method sampling in the 49.5-inch 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 hour 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.

2.3.1.2 Nickel Plating Operation

The Naval Aviation Depot utilizes two electroless nickel tanks located in Building 472. The electroless nickel 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 inches.

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

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

2.3.1.3 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 inches. Stack temperature is slightly elevated at a temperature of 105 degrees Fahrenheit. Access to the test ports for the reference method 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.

2.3.2 Tooele Army Depot (TEAD)

An initial test at Tooele Army Depot's prototype APE 1236M2 munitions deactivation furnace 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 Tooele 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 assure a measureable amount of selected metals in the stack gas, the source was spiked with three different concentrations (low, medium, and high) of cadmium, chromium, nickel, lead, and mercury compounds by using a compressed air aspirator and a peristaltic pump with prepared solutions of chromium, cadmium, nickel, lead, and mercury 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 (CARB's) Independent Contractor Program, performed EPA Method 29 reference method stack sampling. West Coast Analytical Service performed analytical work on the samples collected by PES.

The number of traverse points required (6 on each of 2 diameters, 90 degrees apart) and their locations are specified in EPA Method 1. For each test, the ABF-LIPS instrument collected a sample concurrently with the reference method for multiple metals.

2.4 Sampling/Monitoring Procedures

The experimental design is dictated by Performance Specification 10 (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 reference method, EPA Method 29. This comparative accuracy is termed relative accuracy (RA). Acceptable results for RA per PS10 are values within $\pm 20\%$ of the reference method result. Data quality objectives and measurement parameters applied to these field tests are summarized in Table 2-1. The full specification for PS-10 is included as Appendix A.

ABF-LIPS was operated concurrently with the reference method, EPA Method 29. The reference method 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 reference method were coordinated so that results from ABF-LIPS could be averaged to correspond with the time-integrated sample collected by the reference method. 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 minutes to complete, depending on the anticipated metal concentrations, with half-hour to one-hour setup/breakdown intervals. Samples from the reference method 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.

2.4.1 NADEP Test

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

A time-integrated filter sample was taken by the EPA reference method (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 6-point or a 12-point sampling configuration similar to the EPA RM method does. Since the ABF-LIPS measurement cycle is shorter than 6 minutes, 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 (standard deviation 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 reference methods. Source testing for hexavalent chromium was conducted in triplicate on the common exhaust of both composite mesh pad systems by USEPA Method 306, and source testing for cadmium, chromium, and nickel was conducted concurrently by USEPA Method 29. Two methods were chosen to compare reference method results for chromium.

Source testing for cadmium, chromium, and nickel was conducted in quadruplicate on the exhaust of the mesh pad from the electroless nickel 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 mercury) 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.

2.4.1.1 Metals Spiking

Two ultrasonic particle generators were used at NADEP to spike aerosol particles embedded with metals into the exhaust flow prior to the sampling location. ORNL tested these generators and found that the droplet sizes were about 1.7 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 were injected into the ducts via the ultrasonic nebulizers. The salts are listed in Table 2-2.

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 2-2. 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-mL volume was prepared for each of the three solutions that were designated as L for low strength, M for medium, and H for High strength.

Spiking Solution Strengths	Ni	Cr	Cd	Soln Symbol	Units
Low	330	150	153	L	$\mu\text{g/L}$
Mid	702	601	601	M	$\mu\text{g/L}$
High	2,727	6,000	6,003	H	$\mu\text{g/L}$
Date\Run Number	1	2	3	4	Location
June 16, 2003	M				Cr site
June 17, 2003	M	H			Cr site
June 18, 2003	Baseline	L	M	H	Ni Bath
June 19, 2003	Baseline	L			Kirk site
June 20, 2003	M	H			Kirk site

Table 2-2. Solution concentrations of spiked metals (top rows) and run schedule for NADEP listing spiking concentrations (bottom three rows).

2.4.1.2 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 EPA 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 nickel 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 Kirk site 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 reference methods for total chromium and multiple metals.

2.4.1.2.1 Total Chromium Reference Method Sampling

Total chromium was measured using EPA Method 306 (reference method). The samples were extracted through a glass nozzle, a Teflon union, a 36-60" glass-lined stainless steel probe, a short length of 1/8" Teflon tubing from the probe to the first impinger, two Greenburg-Smith impingers each charged with 100 mls of 0.1N sodium bicarbonate solution, an empty impinger, an impinger filled with silica gel, a 30-foot 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 minutes at 5 minutes per point (24 points total) generating a sample size of about 90 cubic feet through the train. Three test runs were made. Field data was recorded on the data sheets shown in Appendix B, which also details 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 (EPA 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 3rd 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 in order 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 chromium determinations were made by inductively coupled plasma mass spectrometry (ICP/MS). The minimum detection level of the analytical procedure for total chromium, CrT, was 0.2 ug/L. A sample submittal/chain of custody sheet was completed when the samples were submitted. The laboratory analysis report is included in Appendix B.

2.4.1.2.2 Multiple Metals Reference Method Sampling

Multiple metals were measured by using EPA Method 29. The samples were extracted through a glass nozzle, a Teflon union, a 36-60" glass-lined stainless steel probe, a glass fiber filter in a glass housing, a short length of $\frac{3}{8}$ " Teflon tubing from the probe to the first impinger, two Greenburg-Smith impingers each charged with 100 mls of 5% nitric acid/10% hydrogen peroxide solution, an empty impinger, an impinger filled with silica gel, a 30-foot 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 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 72-120 minutes at 3-5 minutes per point (24 points total) generating a sample size of about 54-90 cubic feet through the train. Three to four test runs were made. Field data was recorded on the data sheets shown in Appendix B, 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 (EPA 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 3rd 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 in order 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 mercury) were made by inductively coupled plasma mass spectrometry (ICP/MS). A sample submittal/chain of custody sheet was completed when the samples were submitted. The laboratory analysis report is included in Appendix B.

2.4.2 Tooele Army Depot Testing

The tests at TEAD were performed using the prototype munitions deactivation furnace, APE 1236M2, with no feed (since lead 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 reference method sampling point.

2.4.2.1 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 water in 32 gallon plastic tubs. DI water was produced on site using an industrial 3-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 feet downstream of the afterburner. Figure 2-7 shows the platform used to support the spiking equipment.



Figure 2-7. 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 reference method sampling commenced.

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

The test was run in quadruplicate at each of 3 spiking concentrations - low, medium, and high. Five metals were spiked: cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni), and mercury (Hg). Target concentrations for the spike metals in the stack are shown in Table 2-3. These concentration levels were selected based on those used in previous CEM 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 2-3. Target concentrations for spiked metals in flue gas at TEAD.

ABF-LIPS was set up on the high platform of the exhaust stack, and the reference method equipment was located on the lower platform, approximately 10 feet 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 degrees apart. Photos of the instrumentation are included as Figures 2-8 through 2-11.



Figure 2-8. 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 2-9. 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 2-10. ABF-LIPS instrument (cube structure at left) and laptop used for control and data storage at TEAD during September 2005 test.



Figure 2-11. 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.

2.4.2.2 Reference Method Multiple Metals Sampling

Multiple metals were measured at TEAD using reference method EPA Method 29. Samples were extracted through a glass nozzle, a Teflon union, a 36" glass-lined stainless steel probe, a quartz filter in a glass housing, a set of Greenburg-Smith impingers, a 30-foot 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 mls of 5% nitric acid/10% hydrogen peroxide solution, the third impinger was empty, the fourth and fifth

impingers were each charged with 100 mls 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 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 84 minutes at 7 minutes per point (12 points total) generating a sample size of about 75 cubic feet through the train. Twelve test runs were made: four at each of three spiking levels. Field data was recorded on the data sheets shown in Appendix B, 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 (EPA 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 3rd 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 mls of 8N hydrochloric acid and the rinse was placed in a 250-ml amber glass bottle along with 200 mls 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 in order 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 chromium, cadmium, lead, and nickel were made by inductively coupled plasma mass spectrometry (ICP/MS). Mercury 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 B.

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.

2.5 Analytical Procedures

EPA Method 301, as specified by EPA, is to be used whenever a source owner or operator proposes a test method to meet U.S. Environmental Protection Agency requirement 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 EPA method. EPA Performance Specification 10 (PS-10) is a specific guidance to Method 301 which describes performance criteria for multi-metal CEMs.

PS-10 is to be used to evaluate the acceptability of multi-metals continuous emission monitoring systems (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: 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). The method compares a standard reference method (EPA Method 29) with the instrument to be validated. A minimum of nine pairs of data are collected on 2 or more metals, and the method undergoing validation must be accurate to within $\pm 20\%$ of the reference method. PS-10 is included as Appendix A.

EPA 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. EPA 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 one- to three-hour 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 2.4.

3 PERFORMANCE ASSESSMENT

3.1 Performance Data

3.1.1 NADEP

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

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 C.

3.1.1.1 Chromium Plating Reference Method Source Test

Table 3-1 summarizes the results of the chromium testing by EPA Method 306 on the Enforcer III exhaust. The spiking levels for the three test runs were: none, medium, and high, respectively (the low chromium run was aborted due to failure of the spiking method at an unknown point in the run). The total chromium concentrations for the three EPA 306 test runs were 0.00017, 0.00012, and 0.00096 mg/dscm, respectively. Cumulative run times of sample collection were 120 minutes; start and stop times span greater periods because some time is required for probe repositioning during transect shifts. Results are shown graphically in Figure 3-1 (with results from Method 29, described in the following paragraph). The total chromium emission rates for the three EPA 306 test runs were 9.5, 6.6, and 53.2 mg/hr, respectively.

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, sq. ft.	13.6	13.6	13.6
Flow Rate, ACFM	34,600	34,700	34,700
Flow Rate, DSCFM	32,800	32,900	32,700
Moisture, % v/v	1.8	1.8	2.1
<u>Total Chromium</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	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

Table 3-1. Reference method results by EPA Method 306 for chromium plating exhaust, NADEP 2003.

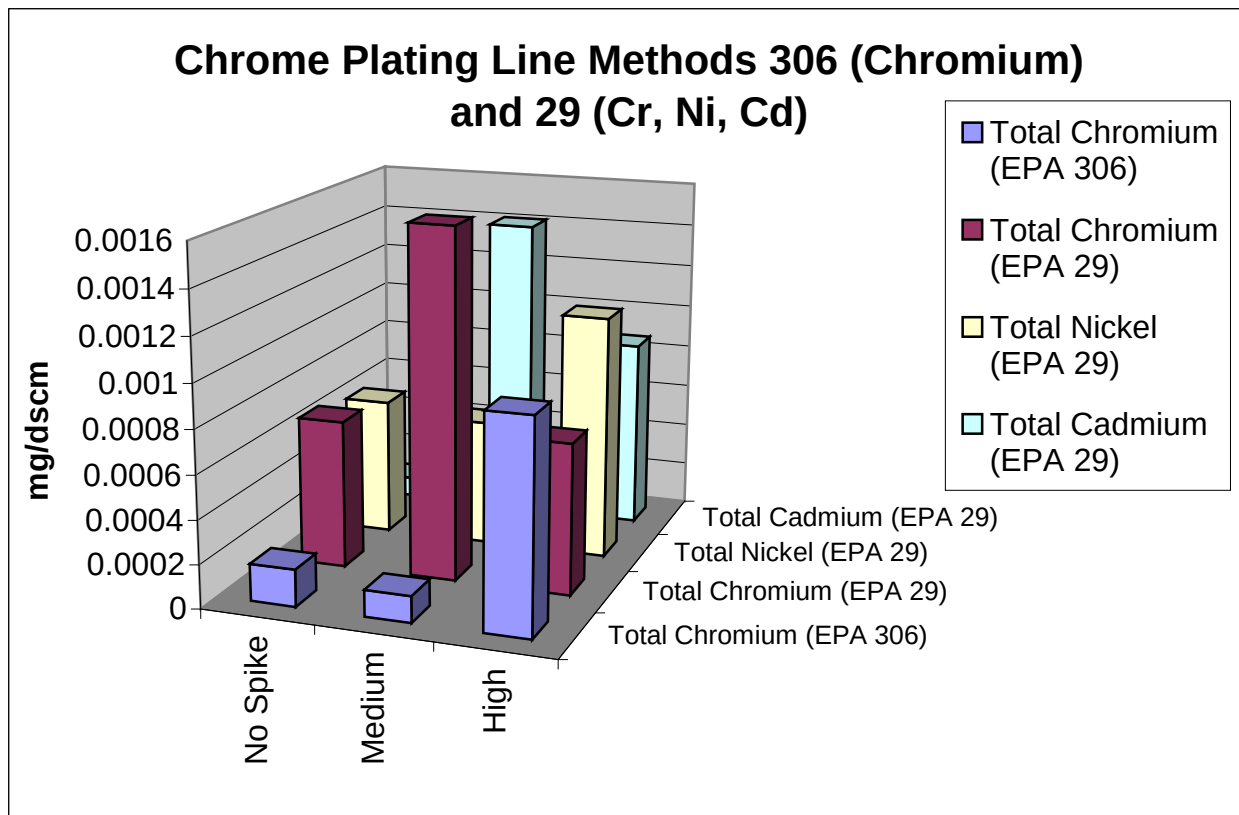


Figure 3-1. Comparison of results of reference method testing using two different methods (EPA Methods 306 and 29) simultaneously for chromium showing disparity of results (two front-most rows). Nickel and cadmium results from Method 29 are also shown. Chrome plating bath exhaust at NADEP, 2003.

Table 3-2 summarizes the results of the metals testing by EPA Method 29 made on the Enforcer III exhaust concurrently with the EPA Method 306 sampling. The total chromium concentrations for the three EPA 29 test runs were 0.00068, 0.00116, and 0.00069 mg/dscm, respectively. Results are shown graphically in Figure 3-1. The total chromium emission rates for the three EPA 29 test runs were 39.3, 66.6, and 39.8 mg/hr, respectively. The total nickel concentrations for the three EPA 29 test runs were 0.00063, 0.00058, and 0.00112 mg/dscm, respectively. The total nickel emission rates for the three EPA 29 test runs were 36.5, 33.2, and 64.5 mg/hr, respectively. The total cadmium concentrations for the three EPA 29 test runs were 0.00009, 0.00141, and 0.00087 mg/dscm, respectively. The total cadmium emission rates for the three EPA 29 test runs were 5.2, 80.9, and 50.0 mg/hr, respectively. Except for the cadmium 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.

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
<u>Flue Gas</u>			
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, sq. ft.	13.6	13.6	13.6
Flow Rate, ACFM	35,500	35,400	35,800
Flow Rate, DSCFM	33,900	33,700	34,000
Moisture, % v/v	1.6	1.7	1.7
<u>Metals</u>			
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	110.2	108.0	110.2
Isokinetic Rate, %	100.7	99.4	100.5
Concentration, mg/dscm			
Total Chromium	*0.00068	*0.00116	*0.00069
Total Nickel	*0.00063	*0.00058	*0.00112
Total Cadmium	*0.000090	0.00141	0.00087
Emission Rate, mg/hr			
Total Chromium	*39.3	*66.6	*39.8
Total Nickel	*36.5	*33.2	*64.5
Total Cadmium	*5.2	80.9	50.0

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

Table 3-2. Reference method results by EPA Method 29 for chromium plating exhaust, NADEP 2003.

3.1.1.2 Nickel Plating Bath Exhaust Reference Method Source Test

Table 3-3 summarizes the results of the metals testing by EPA Method 29 made on the nickel tank mist eliminator exhaust. The spiking levels for the four test runs were: none, low, medium, and high, respectively. The total chromium concentrations for the four EPA 29 test runs were 0.00025, 0.00504, 0.00397, and 0.00653 mg/dscm, respectively. The total chromium emission rates for the four EPA 29 test runs were 16.3, 32.4, 25.8, and 42.2 mg/hr, respectively. Results are shown graphically in Figure 3-2. The total nickel concentrations for the four EPA 29 test runs were 0.00402, 0.00291, 0.00291, and 0.00309 mg/dscm, respectively. The total nickel emission rates for the four EPA 29 test runs were 26.0, 18.8, 18.9, and 20.0 mg/hr, respectively. The total cadmium concentrations for the four EPA 29 test runs were 0.00045, 0.00059, 0.00125, and 0.00194 mg/dscm, respectively. The total cadmium emission rates for the four EPA 29 test runs were 2.9, 3.8, 8.1, and 12.6 mg/hr, respectively. On all of the chromium runs and the second cadmium 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.

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, sq. ft.	3.14	3.14	3.14	3.14
Flow Rate, ACFM	3,990	3,970	4,010	4,010
Flow Rate, DSCFM	3,800	3,790	3,820	3,800
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	77.08	45.66	46.97	45.34
Isokinetic Rate, %	100.1	99.0	101.1	98.0
Concentration, mg/dscm				
Total Chromium	*0.00025	*0.00504	*0.00397	*0.00653
Total Nickel	0.00402	0.00291	0.00291	0.00309
Total Cadmium	0.00045	*0.00059	0.00125	0.00194
Emission Rate, mg/hr				
Total Chromium	*16.3	*32.4	*25.8	*42.2
Total Nickel	26.0	18.8	18.9	20.0
Total Cadmium	2.91	*3.81	8.11	12.6

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

Table 3-3. Reference method results for nickel plating exhaust, NADEP 2003.

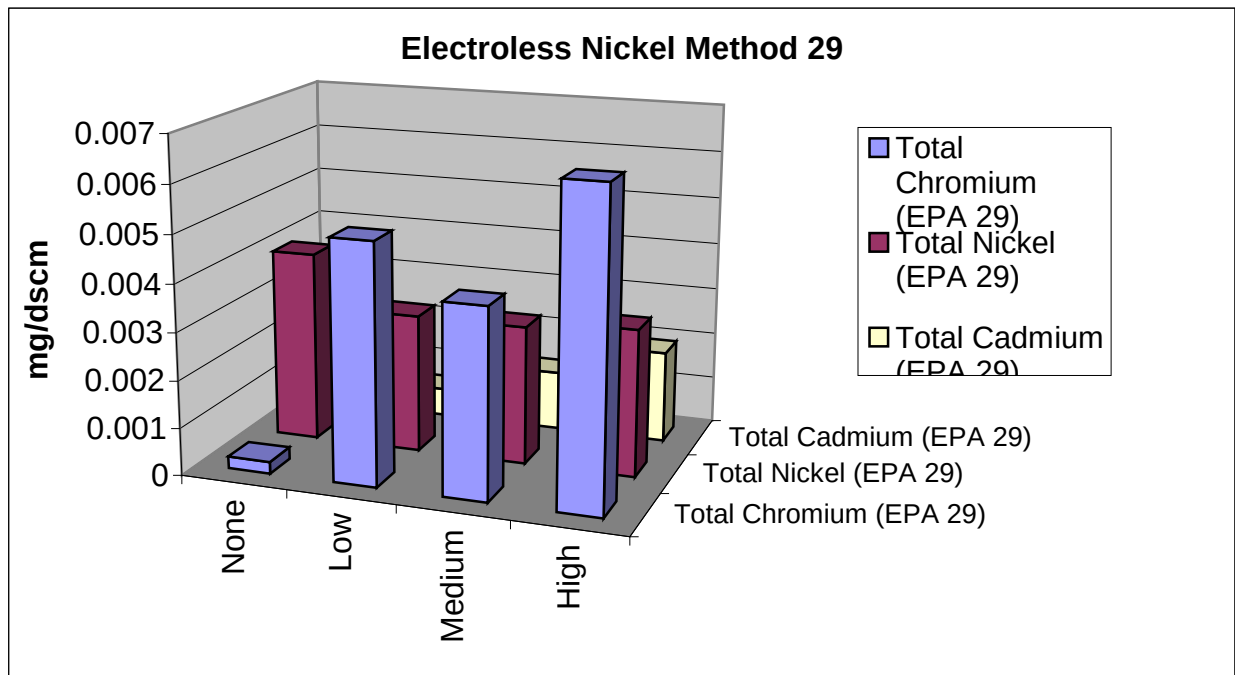


Figure 3-2. Electroless nickel plating bath exhaust stack Method 29 results during baseline (no spiking - none), and after spiking three concentrations of metals (low, medium, high).

3.1.1.3 Kirksite Furnace Exhaust Reference Method Source Test

Table 3-4 summarizes the results of the metals testing by EPA 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 antimony 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 3-3.

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, sq. ft.	6.30	6.30	6.30	6.30
Flow Rate, ACFM	16,500	16,500	16,200	16,400
Flow Rate, DSCFM	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
Sample Volume, DSCF	83.90	50.42	49.65	50.05
Isokinetic Rate, %	100.3	100.4	99.4	98.9
Concentration, mg/dscm				
Total Chromium	*0.00151	*0.00262	*0.00449	*0.00623
Total Nickel	*0.00052	*0.00099	*0.00105	*0.00118
Total Cadmium	*0.00013	*0.00020	*0.00018	*0.00044
Total Antimony	0.00037	*0.00013	0.00144	*0.00010
Total Beryllium	*0.00022	*0.00020	*0.00034	*0.00067
Total Copper	*0.00160	*0.00125	*0.00358	*0.00214
Total Lead	*0.00797	*0.00689	*0.00472	*0.00482
Total Manganese	*0.00006	*0.00043	*0.00037	*0.00100
Emission Rate, mg/hr				
Total Chromium	*40.1	*69.7	*119	*167

Total Nickel	*13.9	*26.2	*27.7	*31.7
Total Cadmium	*3.68	*5.20	*4.62	*11.7
Total Antimony	9.83	*3.51	38.0	*2.70
Total Beryllium	*5.92	*5.20	*8.94	*17.9
Total Copper	*42.4	*33.2	*94.5	*57.3
Total Lead	*212	*183	*125	*129
Total Manganese	*1.54	*11.3	*9.76	*26.9

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

Note: Barium and zinc could not be determined due to high filter background.

Table 3-4. Reference method results for Kirksite furnace exhaust, NADEP 2003.

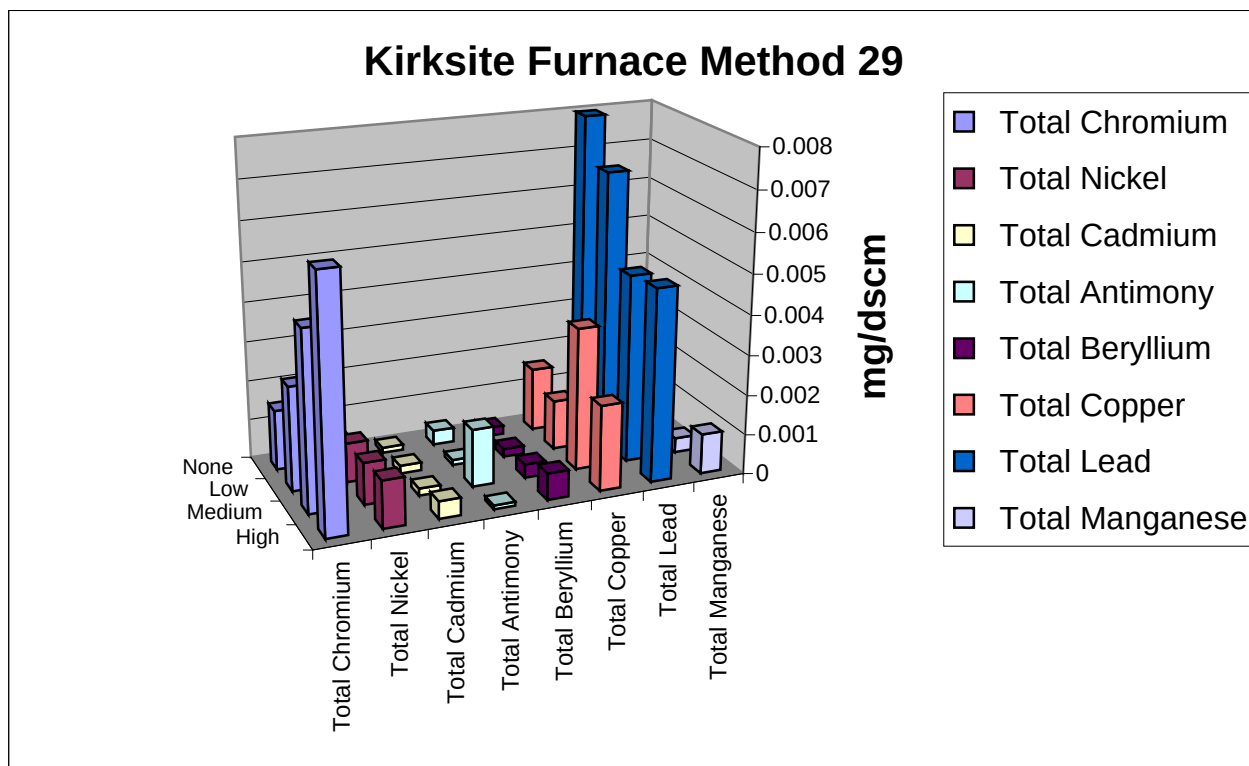


Figure 3-3. Reference method results for Kirksite furnace at NADEP.

3.1.1.4 ABF-LIPS Chromium Plating Bath and Nickel Plating Bath Exhausts

ABF-LIPS measurements at the chromium plating line exhaust and at the electroless nickel 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 3-5 presents the reference method results for the chromium plating exhaust; note that chromium was measured using two EPA Methods, Methods 29 and 306. Agreement between these two standard methods was generally poor (beyond the 20% relative accuracy requirement for new methods per PS-10), suggesting that the reference methods, 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 3-6 presents the reference method results for the electroless nickel exhaust.

Chrome Plating Line (sampled after Enforcer III)			
Reference Method Results (mg/dscm)	No Spike	Medium	High
Total Chromium (EPA 306)	0.00017	0.00012	0.00096
Total Chromium (EPA 29)	0.00068	0.0016	0.00069
Total Nickel (EPA 29)	0.00063	0.00058	0.00112
Total Cadmium (EPA 29)	0.00009	0.00141	0.00087

Table 3-5. Comparison of results for two different reference methods for chromium at chromium plating bath exhaust stack, NADEP. Nickel and cadmium result also shown using Method 29.

Electroless Nickel (sampled after mist pad)				
	None	Low	Medium	High
Total Chromium (EPA 29)	0.00025	0.00504	0.00397	0.00653
Total Nickel (EPA 29)	0.00402	0.00291	0.00291	0.00309
Total Cadmium (EPA 29)	0.00045	0.00059	0.00125	0.00194

Table 3-6. Reference method results at electroless nickel plating bath exhaust stack, NADEP.

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 3-7, together with standard deviations (standard deviations 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 reference method does not have calculable standard deviation. Data are presented graphically in Figures 3-4 through 3-6.

Element	Measurement Method	No Spike	Low Spike	Std. Dev Low	Medium Spike	Std. Dev Med.	High Spike	Std. Dev. High
Cr	EPA Reference Method	0.00151	0.00262		0.00449		0.00623	
Cr	ABF-LIPS		54,068	32,813	86,766	19,187	1,828	2,085
Ni	EPA Reference Method	0.00052	0.00099		0.00105		0.00118	
Ni	ABF-LIPS		12,391	9,174	11,109	3,642	1,868	1,175
Cd	EPA Reference Method	0.00013	0.0002		0.00018		0.00044	
Cd	ABF-LIPS		8,235	7,503	8,794	2,032	6,940	2,765

Table 3-7. Chromium plating bath exhaust measurements using ABF-LIPS and reference method.

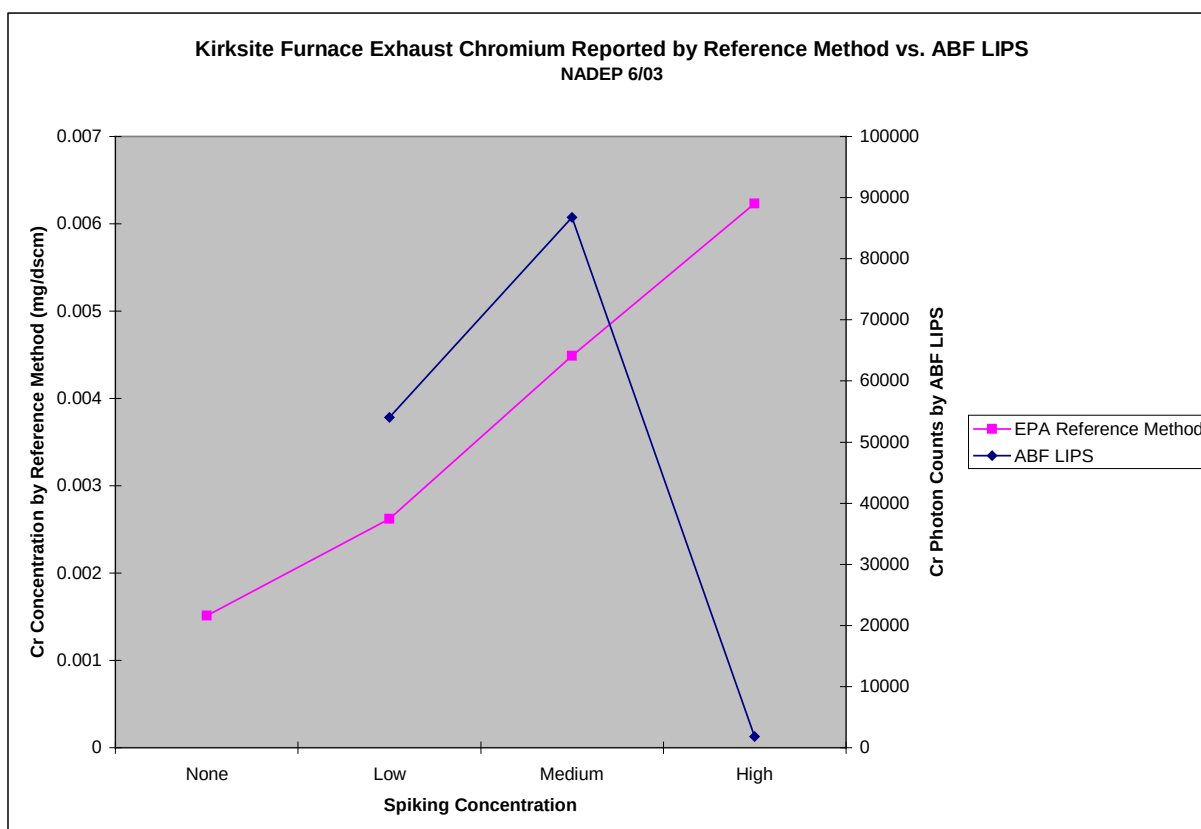


Figure 3-4. ABF-LIPS results vs. reference method for chromium at Kirksite furnace, NADEP.

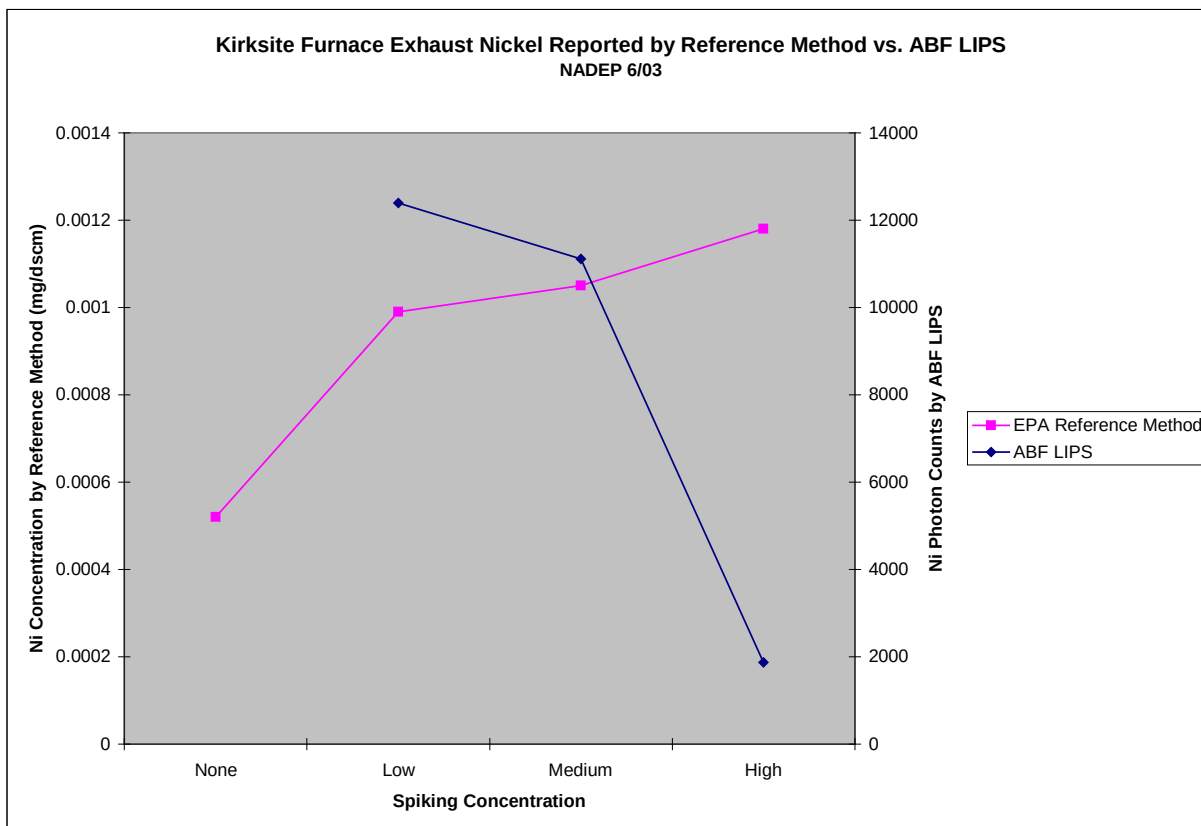


Figure 3-5. ABF-LIPS results vs. reference method for nickel at Kirksite furnace, NADEP.

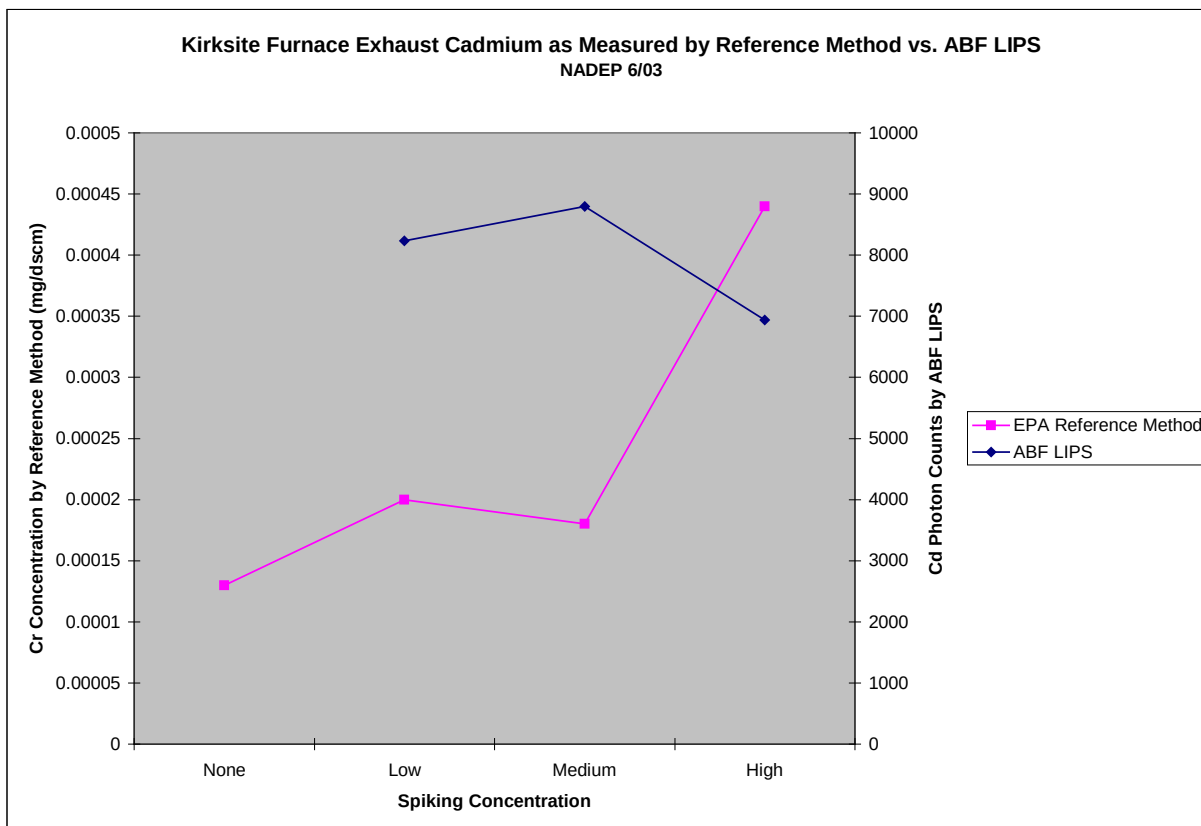


Figure 3-6. ABF-LIPS results vs. reference method for cadmium at Kirksite furnace, NADEP.

3.1.2 TEAD

3.1.2.1 October 2004 Test

The first field test at TEAD in October 2004 was aborted during the first day due to failure of ABF-LIPS associated equipment associated with unexpectedly cold and snowy conditions. Three test runs were completed, but only one of the reference method results were 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 reference method is summarized in Table 3-8. Complete data from that run are included in Appendix B.

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)

Table 3-8. Reference method result for low concentration spike run from October 2004 test at TEAD prior to canceling field test (mg/dscm = milligrams per dry standard cubic meter).

3.1.2.2 September 2005 Test

The second field test at TEAD was carried out September 13-15 2005. Weather conditions were favorable (mostly sunny, 55-75 deg F); as such freezing of standard solutions was not an issue, and the condensation issue on the instrument was remedied by incorporating an air dryer (dessicant). 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 3-9. The results include the average of the quadruplicate runs for both the reference method and ABF-LIPS, together with their standard deviation. Figures 3-7 through 3-11 present the data graphically.

Element	Measurement Method	Low Spike	Std. Dev.	Medium Spike	Std. Dev.	High Spike	Std. Dev.
Cr	EPA 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	EPA 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	EPA 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	EPA 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	EPA 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

Table 3-9. Results of September 2005 field test at TEAD comparing ABF-LIPS and reference method.

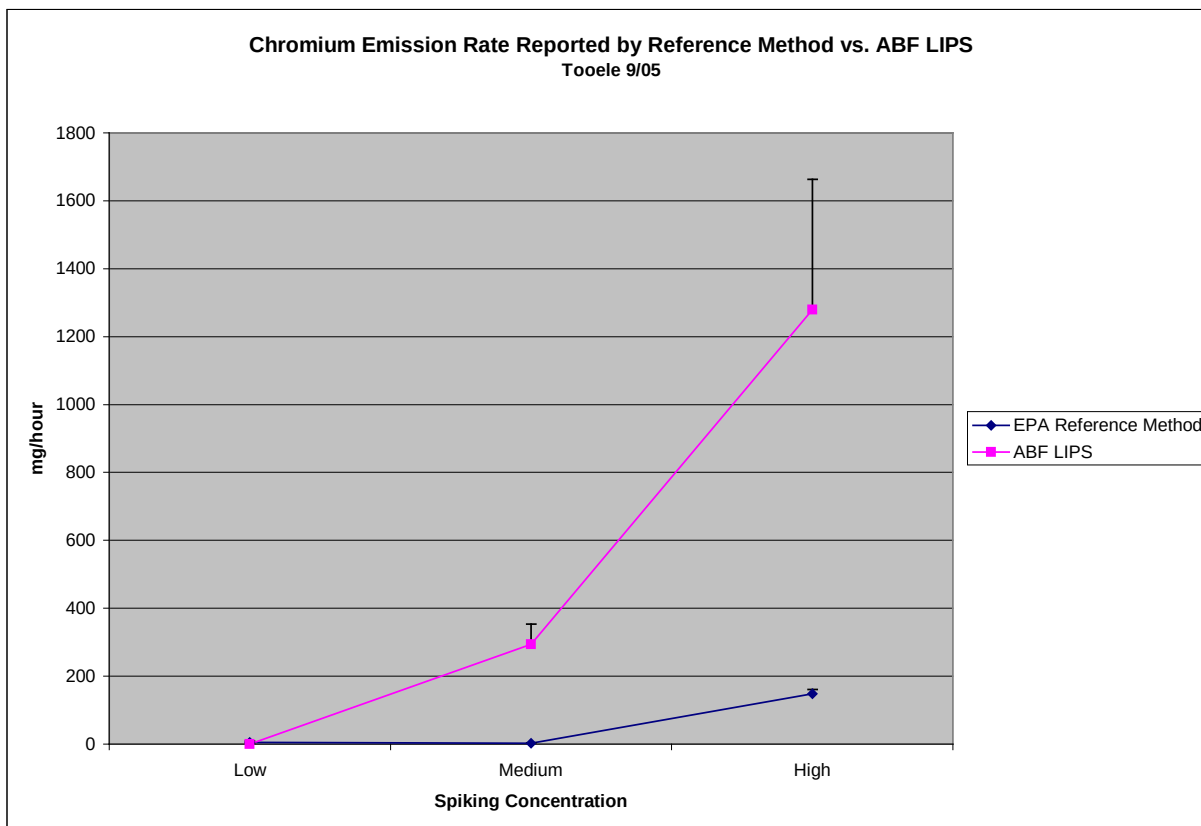


Figure 3-7. Chromium emission rates, with error bars representing one SD (only positive half shown) as measured by ABF-LIPS and the reference method at TEAD.

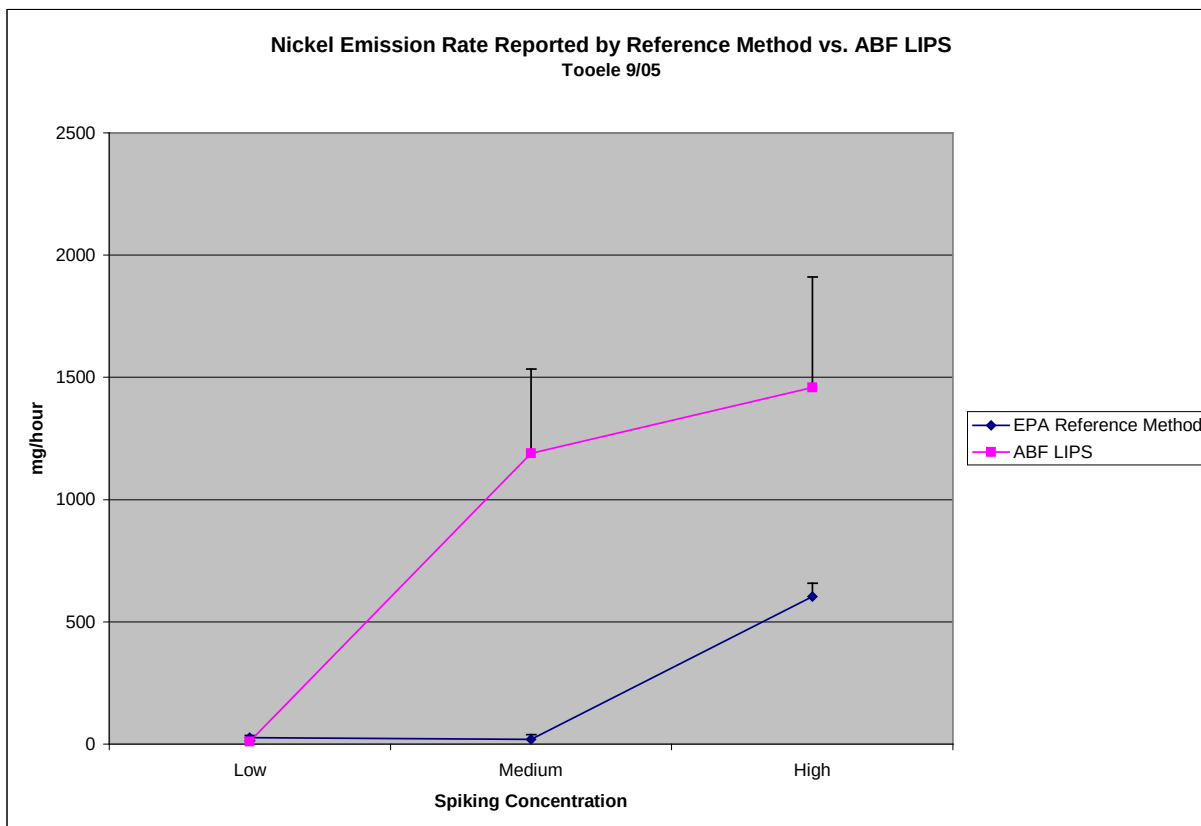


Figure 3-8. Nickel emission rates, with error bars representing one SD (only positive half shown) as measured by ABF-LIPS and the reference method at TEAD.

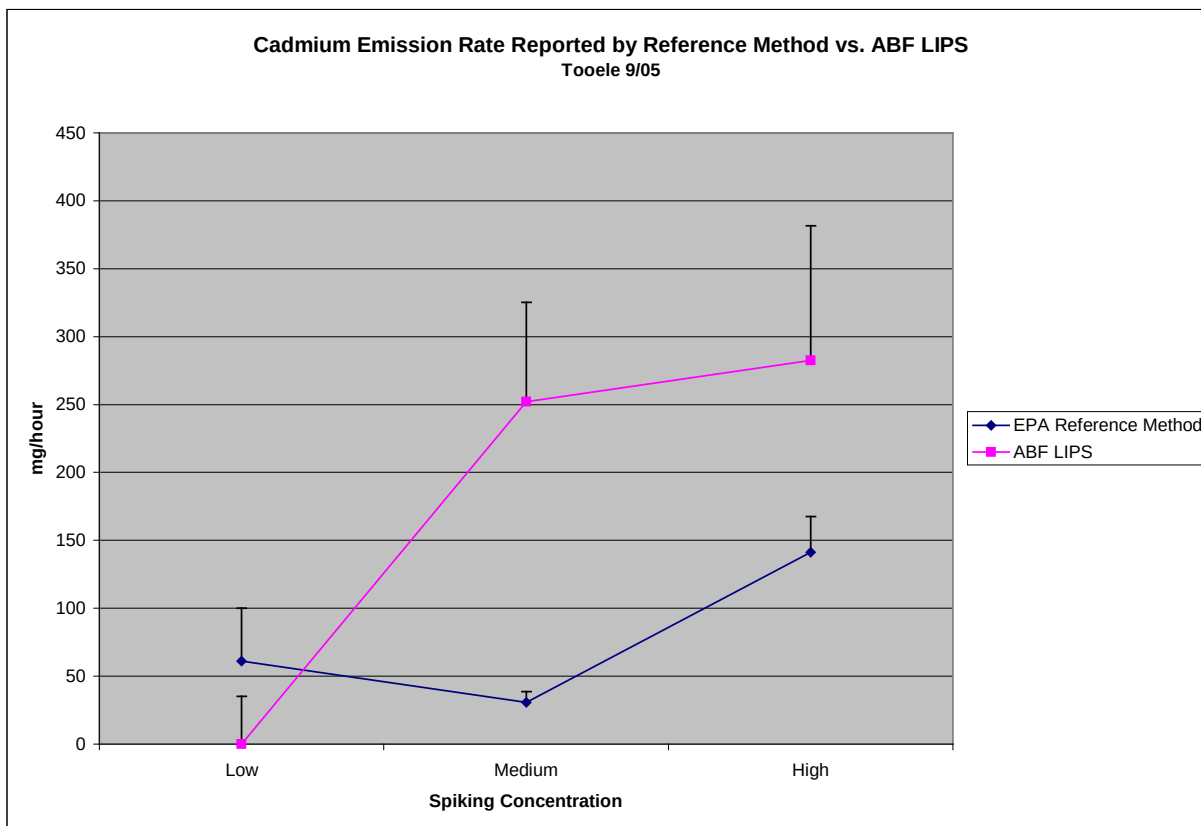


Figure 3-9. Cadmium emission rates, with error bars representing one SD (only positive half shown) as measured by ABF-LIPS and the reference method at TEAD.

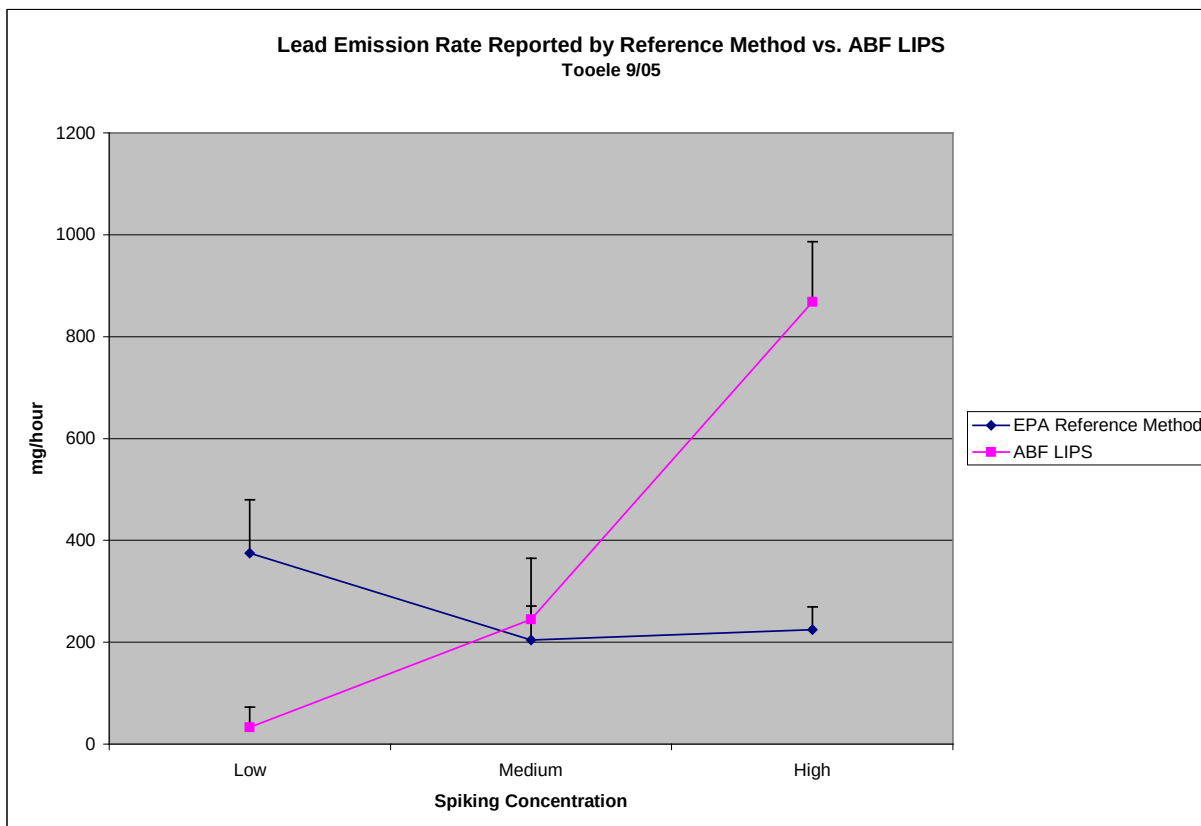


Figure 3-10. Lead emission rates, with error bars representing one SD (only positive half shown) as measured by ABF-LIPS and the reference method at TEAD.

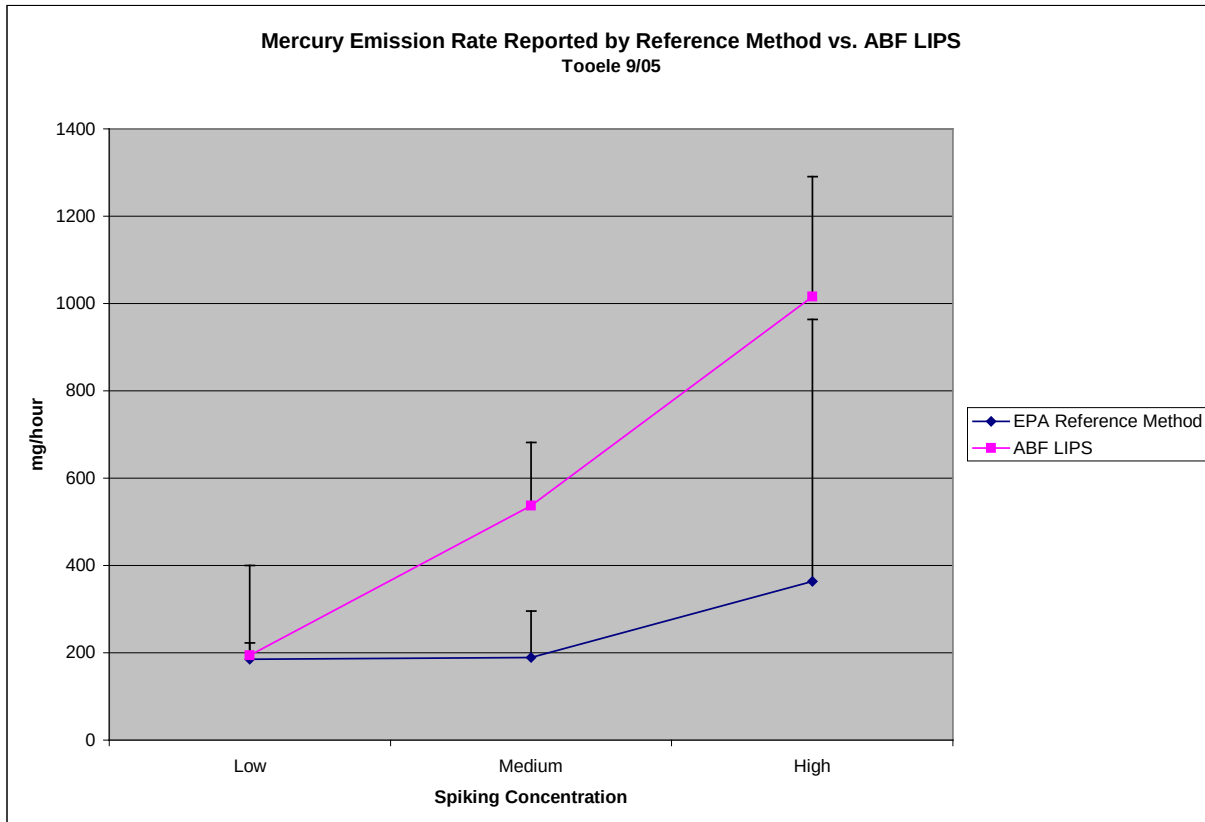


Figure 3-11. Mercury emission rates, with error bars representing one SD (only positive half shown) as measured by ABF-LIPS and the reference method at TEAD.

3.2 Performance Criteria

Performance Specification 10 (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:

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

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

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

value). The CEMS zero point for each metal shall not drift by more than 5 percent of the emission standard for that metal.

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.

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

Table 3-10 lists the performance criteria and whether they were achieved during the tests.

Performance Objective	Metric	Success Criteria	Data Requirements	Notes	Objective Achieved?
Relative Accuracy (bias)	Result compared to reference method	+/-20%	9 data pairs minimum at 3 levels	12 data pairs at 3 levels were collected	No
2 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 CEM only for metals that are tested	Cd, Cr, Ni, Pb, and Hg were monitored in this field test	Yes
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 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 mins.	See note	For ABF-LIPS this is a near-instantaneous figure (milliseconds)	Yes
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) 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	10X the Standard Deviation at the blank level				Yes

Performance Objective	Metric	Success Criteria	Data Requirements	Notes	Objective Achieved?
Capability in Various Environments and Conditions	Exposure to various climates and source operating conditions should not impact data quality			Tested at 3 separate geographic facilities, some outdoor, and various sources at some facilities	Difficulties in cold climates, otherwise performed reasonably well in various conditions
Ruggedness, User-Friendliness, Ease of Setup	Time required for setup, operation learning, and troubleshooting				Setup was less than one hour; only operator was developer

Table 3-10. Performance criteria and result.

3.3 Performance Assessment

3.3.1 NADEP 2003

ABF-LIPS measurements for the chromium plating line exhaust and the electroless nickel 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 reference methods used at the chromium plating line exhaust, EPA 29 and 306, had poor agreement, with a relative accuracy beyond that allowed for new CEMS technologies (20%) per PS-10. The comparison for the two reference methods is presented in Table 3-11.

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

Table 3-11. Comparison of two reference methods for chromium.

Results from the Kirksite furnace suggest that ABF-LIPS measurements are generally anti-correlated to the reference method. Best-fit lines through the data, with R^2 values are shown in Figures 3-12 through 3-14. 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, relative accuracy for these data could not be calculated.

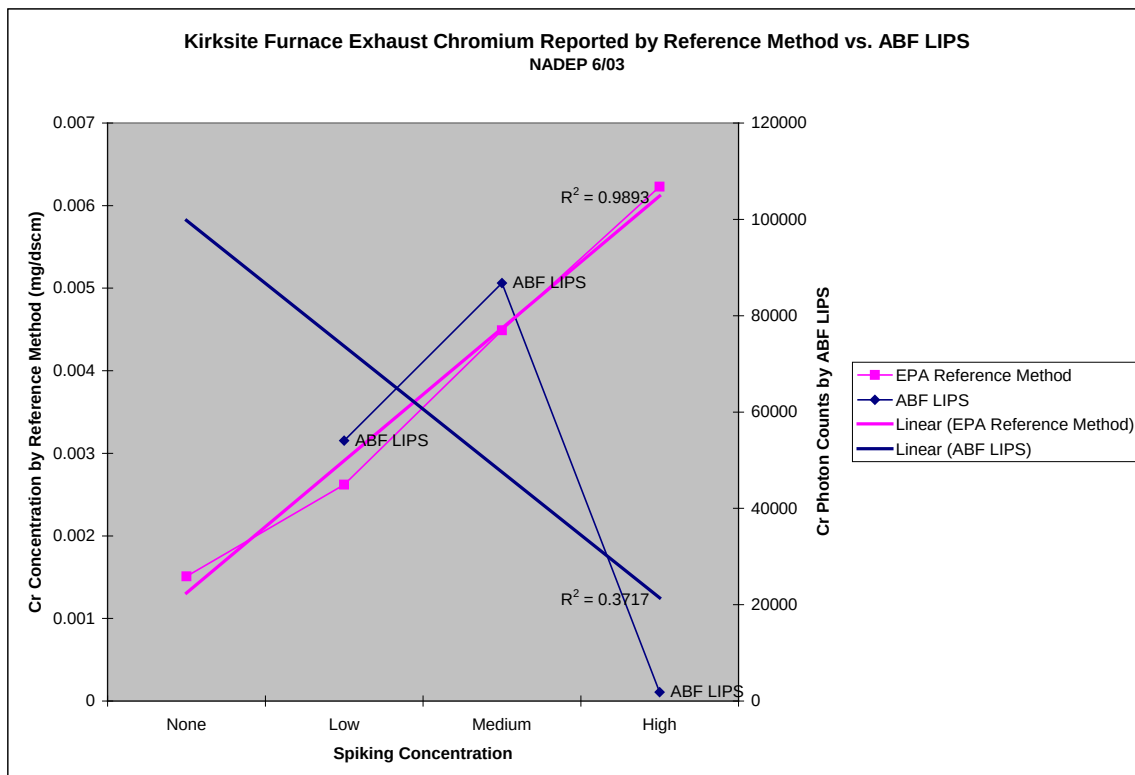


Figure 3-12. ABF-LIPS vs. reference method result for chromium at Kirksite furnace.

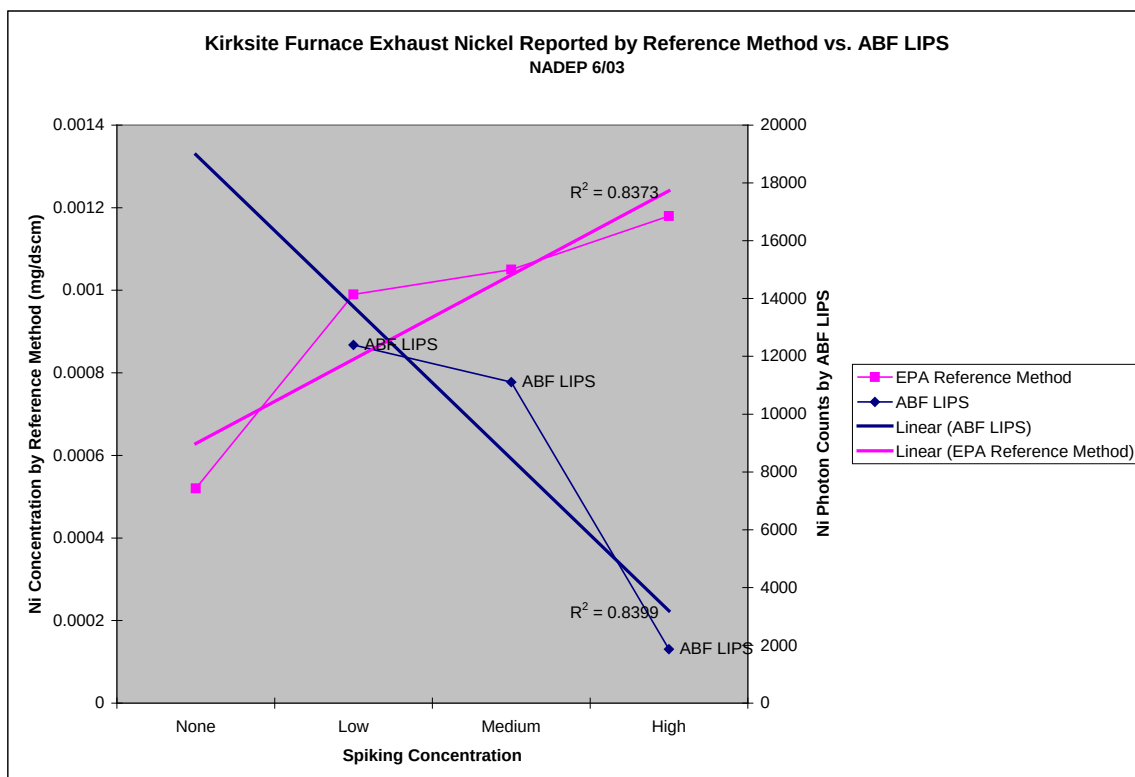


Figure 3-13. ABF-LIPS vs. reference method result for nickel at Kirksite furnace.

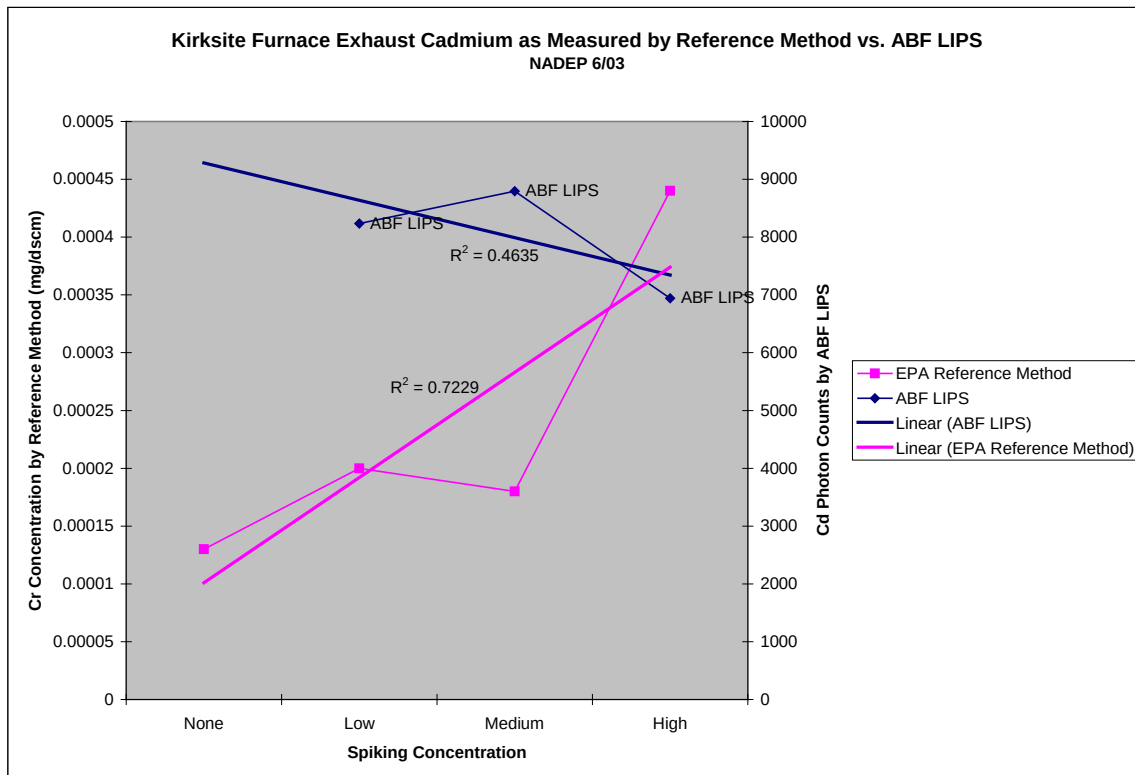


Figure 3-14. ABF-LIPS vs. reference method result for cadmium at Kirksite furnace.

3.3.2 TEAD 2005 Performance Assessment

The relative accuracy of ABF-LIPS to the reference method for the Tooele Army Depot September 2005 field test is presented in Table 3-12.

		Low Spike/ %RA	Std. Dev./ %Variance	Medium Spike	Std. Dev./ %Variance	High Spike	Std. Dev./ %Variance
Cr	EPA Ref. 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	EPA Ref. 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	EPA Ref. 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	EPA Ref. 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	EPA Ref. 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%

Table 3-12. Comparison of ABF-LIPS and reference method results from TEAD, September 2005.

Most runs did not pass the 20% relative accuracy criteria of PS-10. For example, the ABF-LIPS relative accuracy for mercury was 4.8%, 64.7%, and 64.3% for the low, medium, and high spike runs, respectively. However, the standard deviations of the reference method were high as evidenced by the variances shown in the std. dev./ variance columns of Table 3-12. The reference method results for chromium, 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 lead. 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 standard deviations in the reference method results during the first two days of testing (the third day of testing, i.e. high spike runs, had the lowest standard deviations). 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 minutes.

The data presented in Table 3-12 are shown graphically in Figures 3-15 through 3-17.

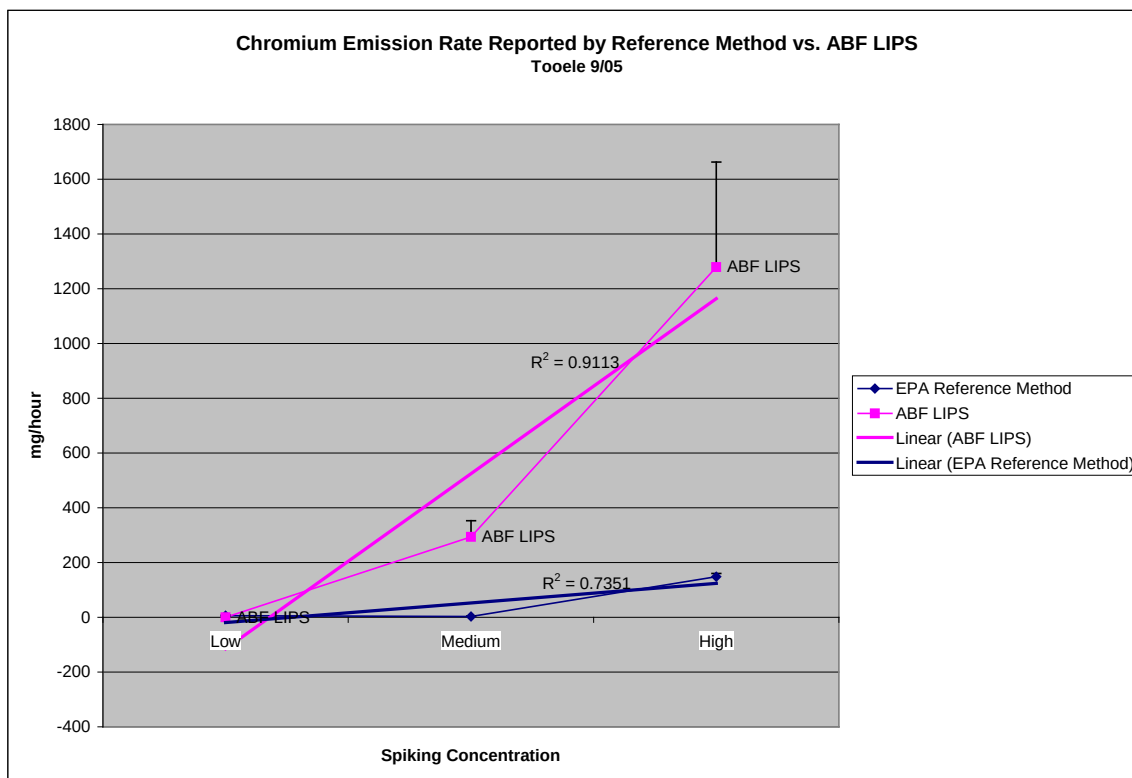


Figure 3-15. ABF-LIPS vs. reference method for chromium at Tooele Army Depot munitions deactivation furnace, September 2005.

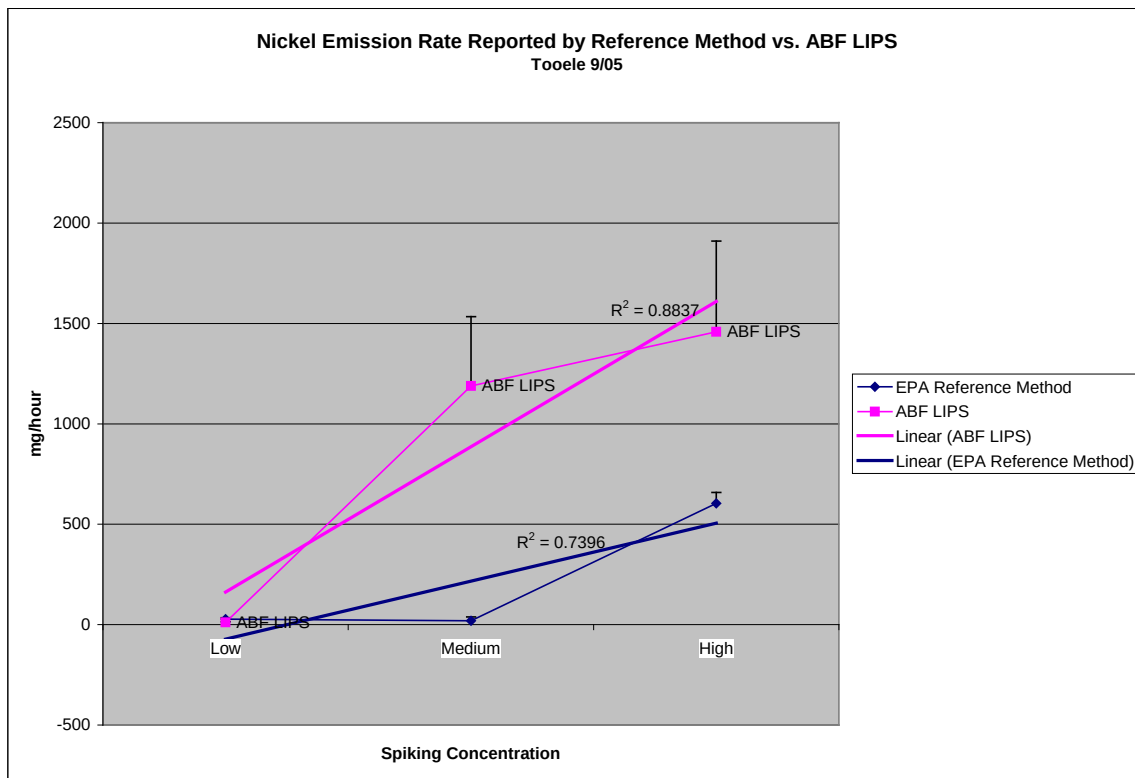


Figure 3-16. ABF-LIPS vs. reference method for nickel at Tooele Army Depot munitions deactivation furnace, September 2005.

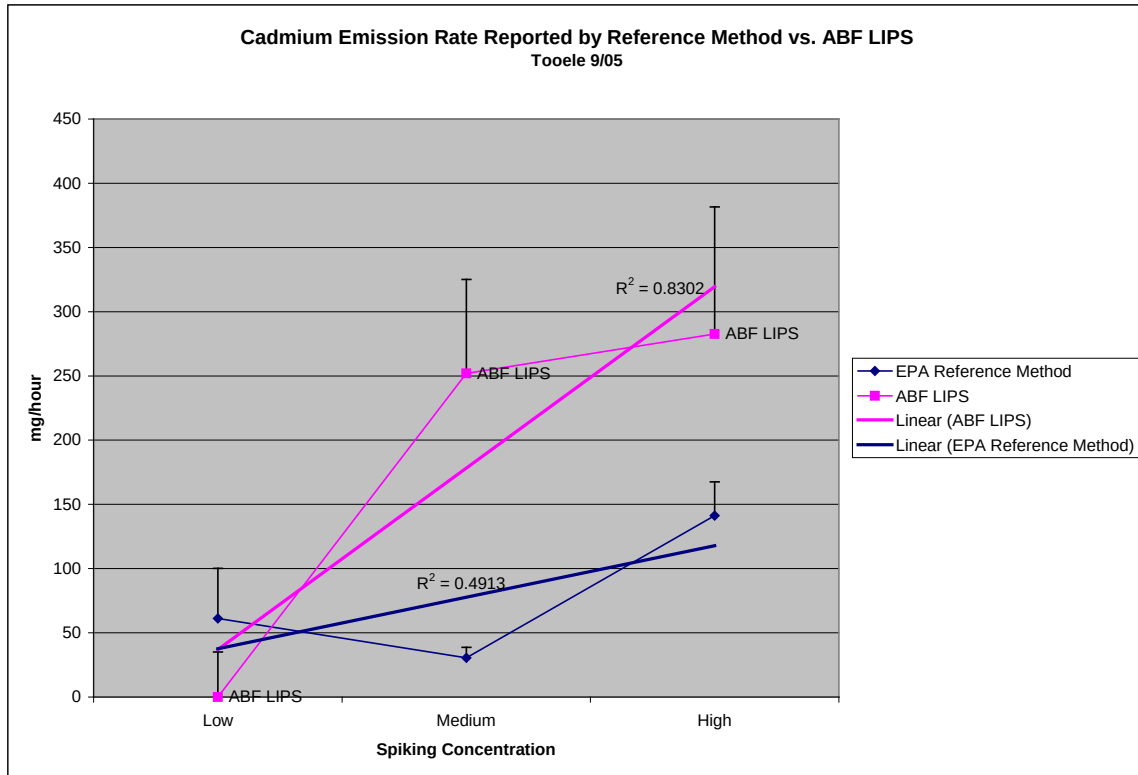


Figure 3-17. ABF-LIPS vs. reference method for nickel at Tooele Army Depot munitions deactivation furnace, September 2005.

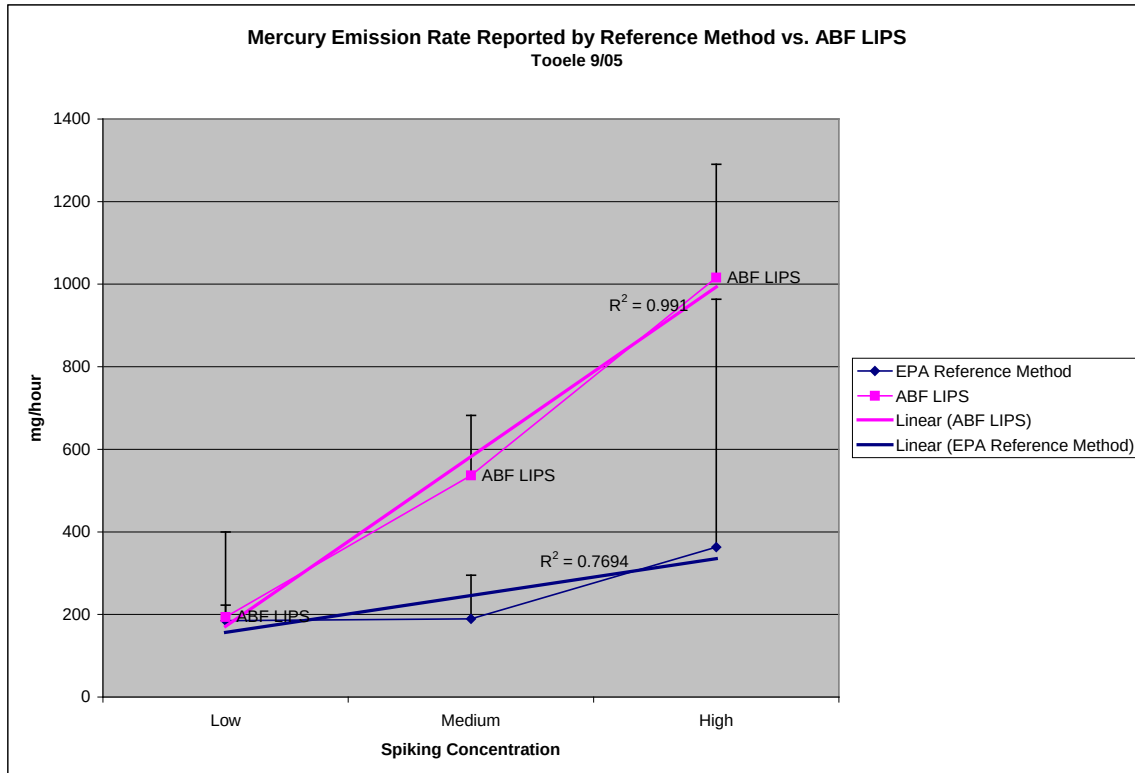


Figure 3-18. ABF-LIPS vs. reference method for mercury at Tooele Army Depot munitions deactivation furnace, September 2005.

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.

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

3.4 Technology Comparison

The standard method used in these studies as a reference method (EPA 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 at this stage of development user-friendly, but clearly was simpler from an operator perspective than that of the reference method. Results were obtained in near real time, with only two minute analysis cycles (vs. the 80-120 minute cycle times of the reference method), 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 set-up to remotely monitor a source,

something the reference method does not lend itself to. Further development of ABF-LIPS will allow remote operation, though the tested version required “hands-on” attention.

4 COST ASSESSMENT

4.1 Cost Reporting

Estimates for ABF-LIPS capital and operating costs are listed in Table 4-1. Since these are rough estimates, a range of costs are given. Operating costs for ABF-LIPS are on an annual basis.

ABF-LIPS Monitoring Costs							
Direct Environmental Activity Process Costs				Indirect Environmental Activity Costs (exisiting 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 assoc. 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	Envr. Mgmt. 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		

Table 4-1. Comparison of ABF-LIPS and reference method results from TEAD, September 2005.

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 processes can incorporate ABF-LIPS as another process unit at marginal cost, estimated to be \$10 to 20K per year.

4.2 Cost Analysis

4.2.1 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 – 85,000 and replacement with a gateable photomultiplier tube plus a narrowband notch filter for an element.

4.2.2 Minor Component Costs

These include the aerosol sampling and focusing unit and comprise a cost on the order of \$7,000.

4.2.3 Software Cost

Software comprises a relatively small cost. Current software was written by researchers at Oak Ridge National Laboratory. Development of ABF-LIPS into a commercial version will require a more "user-friendly" version of the software. The typical cost for a commercial software for an instrument such as the ABF-LIPS is approximately \$5,000-\$8,000 a copy.

4.3 Cost Comparison

Annual sampling of a stack source such as the furnace at Tooele costs \$57k but does not require a capital cost. Capital costs for an ABF-LIPS system capable of measuring multi-metals (all HAP metals) is \$190K to \$455k. Annual O&M costs for ABF-LIPS are projected to be \$14K to \$35K. Assuming the usable life of an ABF-LIPS unit is 10 years, the annualized cost is \$33K to \$80.5K (annual O&M + startup cost/10). Thus ABF-LIPS could save up to \$24k/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 \$23.5K more per year for ABF-LIPS.

5 IMPLEMENTATION ISSUES

5.1 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.

5.2 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.

5.3 Scale-Up

NA

5.4 Other Significant Observations

The existing ABF-LIPS prototype is currently not weather-resistant, and so must be housed indoors in a temperature controlled environment. Further development of the instrument might produce a unit that can be housed in a weathertight 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 reference method 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 deactivation furnace, or a change to the emission

control system, might alter the amount of soot carbon in the flue gas. This could affect the sensitivity of the detector due to absorption due to scatter, 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.

5.5 Lessons Learned

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

5.6 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 (CAAA) Monitoring Requirements for Toxic Release Inventory (TRI) Compounds," and the Army's requirement for "Hazardous Air Pollutant (HAP) and Volatile Organic Compounds (VOCs) 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 \$200k range. Depending on the number, type, and physical arrangement of stacks at a facility, the cost of monitoring by CEM may be multiplied. In addition, consumables and maintenance costs may translate into operational and maintenance (O&M) costs that exceed capital expenditures over some years.

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

Physico-chemical Properties of Aerosols. Larger particles ($D_p > 10 \mu\text{m}$) 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, lead in a munitions deactivation furnace 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, we have identified a private company that has the capability to manufacture and market this technology, Comstock, Inc. Comstock Inc. will be involved in the development and engineering of the hardware/software and in commercialization of this technology. The EPA has also agreed to become a stakeholder on this project. The EPA 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.

5.7 Approach to Regulatory Compliance and Acceptance

In 1990, Congress amended Section 112 of the Clean Air Act (CAA) requiring the EPA to identify and regulate all significant stationary sources that emit any of 189 HAPs. Eleven of these HAPs are metals (antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, nickel, and selenium). Currently, the EPA 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 EPA is developing regulations to limit emissions of the HAP metals from sources such as incinerators and coal-fired power plants, among others. The 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 the EPA (EPA/625/R-97/001, 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 of the EPA 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 EPA approved methods. Further development of ABF-LIPS will be required, however, prior to additional validation testing and eventual regulatory acceptance.

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