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TECHNICAL REPORT
TR-2350-ENV

VALIDATION OF THE AEROSOL BEAM-FOCUSED LASER-INDUCED PLASMA SPECTROMETER (ABF-LIPS) FOR METAL EMISSION CHARACTERIZATION

WP-0213

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March 2010

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From – To)*
31-03-2010	Final Technical Report	January 2002 – February 2010

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Validation of the Aerosol Beam-Focused Laser-Induced Plasma Spectrometer (ABF-LIPS) for Metal Emission Characterization WP-0213	
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)	5d. PROJECT NUMBER
Cheng, M., Oak Ridge National Research Laboratory	ESTCP
Ruiz, N., NAVFAC Engineering Service Center	5e. TASK NUMBER
Kornuc, J., NAVFAC Engineering Service Center	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESSES	8. PERFORMING ORGANIZATION REPORT NUMBER
Naval Facilities Engineering Service Center (NAVFAC ESC) 1100 23rd Avenue EV 31 Port Hueneme, CA 93043	TR-2350-ENV

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITORS ACRONYM(S)
Environmental Security Technology Certification Program (ESTCP) 901 N. Stuart Street, Suite 303 Arlington, VA 22203	ESTCP
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The Aerosol Beam-Focused Laser-Induced Plasma Spectrometer (ABF-LIPS) is a pulsed laser beam focused onto an aerosol sample to ignite a plasma, degrading compounds to their elements, vaporizing them to an unstable, excited state. As atoms return to ground state, light released at element-specific wavelengths can be observed using time-resolved spectroscopy. The ABF-LIPS was tested at the Naval Aviation Depot (NADEP), San Diego, CA and at Tooele Army Depot (TEAD), UT. The NADEP test produced useable data for only one emissions source, but these data did not correlate with spiking levels of the three test metals (Cd, Cr, Ni). The ABF-LIPS was modified prior to TEAD field tests. These data correlated well with spiking levels, but agreement with reference method results was not within the USEPA PS-10 RA acceptance criteria of 20% for any of the five test metals; thus primary performance criteria were not met. Further development of ABF-LIPS is required prior to more validation testing and eventual regulatory acceptance. 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.

15. SUBJECT TERMS

 aerosol beam focused laser spectrometer, ABF-LIPS, metals, Cr, Cr, Ni, continuous emissions monitoring, ESTCP

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Nancy E. Ruiz
U	U	U	U	128	19b. TELEPHONE NUMBER *(include area code)* 805-982-1155

FINAL REPORT

Validation of the Aerosol Beam-Focused Laser-Induced Plasma Spectrometer (ABF-LIPS) for Metal Emission Characterization

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TABLE OF CONTENTS

APPENDICES

LIST OF FIGURES

LIST OF TABLES

LIST OF TABLES *(continued)*

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)

ACKNOWLEDGEMENTS

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 INTRODUCTION

This report describes field validation testing of a novel, real-time, portable CEMS: the Aerosol Beam-Focused Laser-Induced Plasma Spectrometer (ABF-LIPS). ABF-LIPS results are compared with standard methods for HAPS from several real-world sources, and performance and cost considerations are analyzed.

1.1 BACKGROUND

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). Facilities that do not have a CEM typically rely on restrictive operating conditions to promote compliant operations. 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.

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. 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.

1.2   OBJECTIVE OF THE DEMONSTRATION

A portable real-time multi-metals continuous emission monitoring systems (CEMS), the Aerosol Beam-Focused Laser-Induced Plasma Spectrometer (ABF-LIPS) was field-tested at real-world facilities including a metals plating shop, a molten metal casting furnace, and a munitions deactivation incinerator. The performance criteria for the tests included relative accuracy (RA), or the agreement (bias) of the result 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. 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.

The performance 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. The testing was carried out at two DoD facilities on a total of four emission sources. 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 (TEAD'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 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.

1.3 REGULATORY DRIVERS

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.

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)

Carcinogenic Metals	$\mu g/m^3$ (annual limit)	Non-Carcinogenic Metals	$\mu g/m^3$ (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

2   TECHNOLOGY DESCRIPTION

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.

2.1   TECHNOLOGY OVERVIEW

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 2-1. Figures 2-2 and 2-3 illustrate the principles of aerosol focusing and concentration of particles.
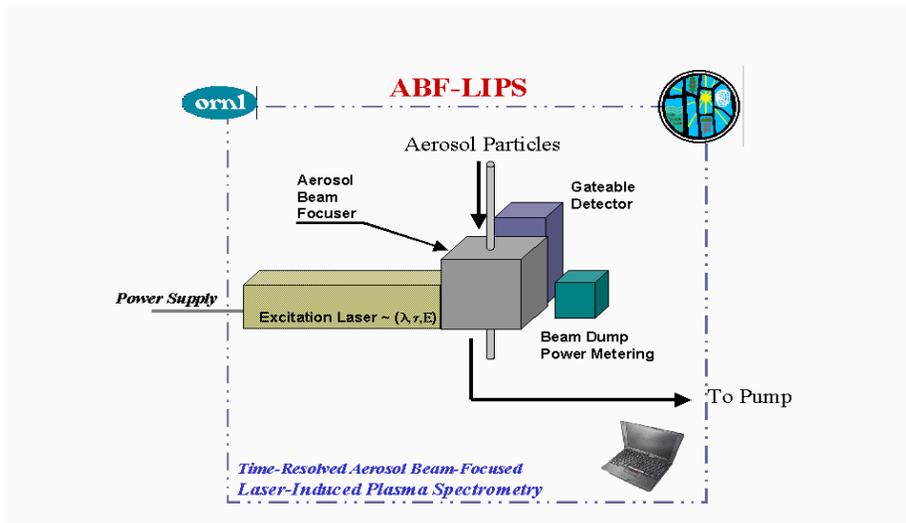
Figure 2-1. Schematic of the Aerosol Beam Focused Laser Induced Plasma Spectrometer (ABF-LIPS).
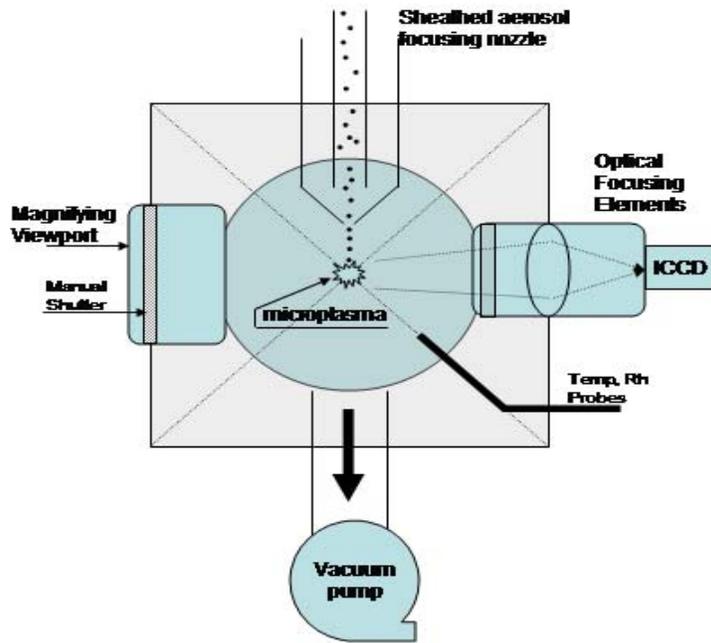
Figure 2-2. Schematic of Aerosol Focusing Process.
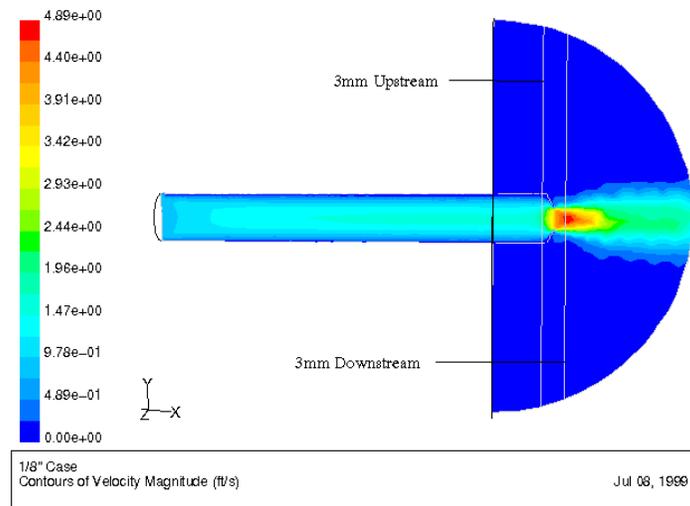
Figure 2-3. Focusing Simulation by Computational Fluid Dynamic (CFD) Modeling.

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.

2.2   TECHNOLOGY DEVELOPMENT

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.

The technology was further developed and subsequently refined in 2000. A field-portable unit, shown in Figure 2-4, 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, housed in a cage to prevent misalignment during transportation in the field. The excess laser energy was discarded to a beam dump at the other end of the cell. The aerosol particles were drawn into the

focusing cell by a piston pump operated at a flow rate approximately 2.5 L/min, and the focusing position was 2 mm from the nozzle exit.

Figure 2-4. ABF-LIPS prototype.

The prototype ABF-LIPS had undergone previous field-testing between 2000 and 2002 using particles from a diesel engine at the National Transportation Research Center at 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.

2.3 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 2-1 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 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. 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.

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

Monitor Feature	ABF-LIPS		TraceAir XRF	SpectroLaser	OceanOptics LIBS2000+	ADA SEA	*	XCEMS
Excitation source	Nd:YAG laser	ICP	X-Ray	Nd:YAG laser	Nd:YAG laser	Nd:YAG laser	N/A	SRF
Electrical enhancement	Yes	No	No	No	No	No	No	
Spectrograph	Echellette	Echellette		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

3   PERFORMANCE OBJECTIVES

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.

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 3-1 further describes the performance criteria, acceptance criteria requirements, procedures/action and notes.

Table 3-1. Data Quality and Quality Assurance Objectives

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

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:

$$RA = \frac{|\bar{d}|}{}$$

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.

4   FACILITY DESCRIPTIONS

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.

4.1   FACILITY LOCATION AND OPERATIONS – 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.

4.1.1   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 4-1. 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 (Stage4), and fourth (Stage5) 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 4-2. 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 4-1. Chromium plating bath operation at NADEP.

Figure 4-2. Sampling port on chromium plating bath exhaust on roof of building at NADEP.

4.1.2 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 4-3). 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 4-3. Electroless nickel plating bath exhaust stack on roof of building at NADEP.

4.1.3 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 4-4. 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 4-4. Kirksite furnace melting pot in hood at NADEP.

4.1.4 Site Conditions – NADEP

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. The weather was mostly sunny and temperatures were in the low 70's and upper 60's. Windy conditions on the final day while testing the Kirksite furnace on a "cherry-picker" platform rig complicated measurements due to swaying.

4.1.5 Site Conditions – 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 with mild weather consisting mainly of sunny skies and temperatures in the 50's in the morning with warming to the low 70's in the afternoon.

4.1.5.1 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.

4.1.5.2 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.

4.1.5.3 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.

4.2 FACILITY LOCATION AND OPERATIONS – 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 munitions deactivation furnace, serving as the high-temperature test facility. The APE 1236M2 DF system, shown in Figure 4-5, 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.

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 $^{\circ}$F while the discharge end ranges from 800-1100 $^{\circ}$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.

The afterburner is designed to raise the temperature of the exhaust gases exiting from the kiln via an 8.7 MM BTU/hr diesel fired burner. 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 $^{\circ}$F to 1400-1600 $^{\circ}$F with a minimum flues gas residence time of 2 seconds.

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 120 ft of 30-inch diameter stainless steel ducting. The ducting is long enough to produce a temperature drop from 1600 $^{\circ}$F at the exit of the afterburner to 1000 $^{\circ}$F prior to entering the bag house. The bag house 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.

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.

The 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 4-6.

Figure 4-5. APE 1232M2 Prototype Munitions Deactivation Furnace Demonstration Site,Tooele Army Depot, Tooele, Utah.

Figure 4-6. APE 1236M2 Furnace Stack, Tooele Army Depot, Tooele, Utah.

4.2.1   TEAD 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).

4.2.2   TEAD Testing and Site Conditions

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.

5   TEST DESIGN

5.1   CONCEPTUAL TEST DESIGN

Real-world sources are configured with pollution control devices and so do not typically provide suitable concentrations of HAPs in the flue exhaust. This requires that sampling take place prior to the pollution control device but this is often precluded by non-laminar flow in the stack due to the proximity of elbows, tees, and other flow disturbances. In lieu of sampling in non-laminar regions, spiking of the exhaust stack with the metals of concern can provide detectable concentration in the linear range of the test instrument, and the stack concentrations can be varied to determine the linearity of response and the lower detection limit.

The general approach in the field demonstrations was to spike the exhausts with a solution of several test metals via a nebulizer to create an aerosol. The solution concentration an flow rate into the stack are known, so a target metal concentration as an aerosol in the gas stream is known.

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 ± 20% of the reference method. PS-10 is included as Appendix B.

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.

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 ± 20% of the reference method result. Data quality objectives and measurement parameters applied to these field tests are summarized in Table 3-1. The full specification for PS-10 is included as Appendix B.

ABF-LIPS was operated concurrently with the reference method, EPA Method 29. The reference method (RM) probes traversed the stacks/ducts per 40 CFR part 60, Appendix A, Method 1, Sections 2.2 and 2.3. Duct diameters were calculated per 40 CFR part 60, Appendix A, Method 1, Section 2.1. Start and stop times for both the ABF-LIPS and the 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.

It is important to note that the reference method results in a time-integrated sample of about one to two hours, whereas ABF-LIPS results in a near-instantaneous "snapshot" reading. Thus, multiple ABF-LIPS readings (currently the instrument is capable of a reading about every six minutes) are taken during a typical one to two hour reference method sampling run. These multiple ABF-LIPS results can be averaged over the course of the test run.

Spiking of the emission stream (stack or duct) is a continuous process during each test run. The nebulizer which delivers the aerosol is turned on prior to each run to achieve steady-state conditions, and continues to deliver the flow through the duration of the run. As such, there is no intended "spike" during each run, rather a continuous elevated concentration of aerosolized metals. ABF-LIPS "sees" these metals in the instant it analyzes a sample, whereas the reference method continuously integrates the metals onto its filtration media during each run.

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 were delivered to an analytical laboratory and results became 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.

5.2   BASELINE CHARACTERIZATION AND PREPARATION

Each facility tested required authorization from the appropriate State regulatory authority. Since metals were going to be spiked following the pollution control devices on each source, the level of emissions needed to comply with operating permits.

Some ducts required that sampling ports be installed, since two methods (ABF LIPS and the reference method) were to be run simultaneously, and porting is typically set up on a duct for a single sampling probe run in two transects 90 degrees apart. To avoid crossing of the ABF LIPS and the reference method probes, additional ports were installed as necessary several feet away from the existing ports. It was assumed that the sampling probe, being about ½ inch diameter,

did not introduce sampling interferences due to the relatively large duct size. The NADEP tests were conducted during normal operations, but the TEAD tests were conducted without ammunition passing through the incinerator, but was operated for the purpose of the ABF LIPS demonstration.

Background concentrations of metals were relatively low in all cases since pollution prevention equipment was operational (except for the Kirksite furnace, where there is no air pollution control device), thus requiring spiking of a metals aerosol to achieve detectable and quantifiable concentrations. In some cases, baseline measurements of some sources were made prior to spiking as described in the following section.

5.3   DESIGN AND LAYOUT OF TECHNOLOGY AND METHODOLOGY COMPONENTS

5.3.1   NADEP Test

The experimental approach at NADEP was to measure three sources by ABF LIPS and the reference method: 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 for the reference method 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 test run, in parallel with multiple measurements (due to the short sampling time) using ABF LIPS. The guidance for continuous emissions multi-metals analyzers, EPA PS-10, specifies that measurements be taken at three concentrations in triplicate, resulting in a total of nine test runs for each source. Twelve test runs were typically made for purposes of better statistical representation and redundancy.

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 electrolesss 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.

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 Kirksite furnace were conducted on the exhaust to atmosphere at roof level.   For each

source, the ABF-LIPS instrument collected a multipoint continuous sample concurrently and in the same plane as the reference methods for total chromium and multiple metals.

Metals spiking was performed by injecting an aerosol from a nebulizer at a point at least 8 duct diameters upstream of the sampling points, but after any pollution control equipment. For the chrome plating line the injection point was in the horizontal ducting coming off of the scrubbers (just off of the roofline of the building), for the nickel plating line nebulizers were located just above the fume collection hoods in the ducting (testing was performed inside the building at this location, prior to pollution control devices on the roof), and for the Kirksite furnace the spiking was performed above the shroud covering the furnace in the ducting.

5.3.1.1   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 salt solutions are listed in Table 5-1.

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 5-2. For the spiking solutions, Ni was produced from $NiCl_2$ salt, Cd was from $CdCl_2$, and Cr was from $K_2Cr_2O_7$ 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.

Table 5-1. Solution concentrations of spiked metals (top rows) and run schedule for NADEP listing spiking concentrations (bottom three rows)

Spiking Solution Strengths	Ni	Cr	Cd	Soln Symbol	Units
Low	330	150	153	L	µg/L
Mid	702	601	601	M	µg/L
High	2,727	6,000	6,003	H	µg/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			Kirksite
June 20, 2003	M	H			Kirksite

5.3.2   TEAD Test

The TEAD methodology was similar to that used at NADEP, that is 4 test runs at each of three concentrations using the reference method in parallel with ABF LIPS measurements. The tests at TEAD were performed using the prototype munitions deactivation furnace, APE 1236M2, with no feed (since lead in ammunition would 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. The sampling point was located several feet prior to the baghouse filter. Photographs in the subsequent subsections depict the injection and sampling points.

Photographs of the test locations with instrumentation are included in Figs. 5-7 through 5-11.

5.3.2.1   Metals Spiking at TEAD

Due to the formation of a precipitate in stock solutions of metals during the first aborted field test at TEAD, the second field test used pre-weighed vials of metals which were dissolved on-site in 20-gallon containers containing DI water. DI water was produced on-site using water filtration canisters. The resulting solution, consisting of dissolved metal salts (same as for NADEP, plus $HgCl_2$) was pumped via a high pressure pump into a nebulizing orifice inserted into the ducting just after the afterburner. Metals concentrations were adjusted for low, medium and high by using pre-prepared vials containing corresponding weights of salts, together with adjustments in pump flow rate. ABF LIPS was used to determine the optimal flow rate, based on response, prior to the actual test runs. Target metals concentrations in the duct are shown in Table 5-2.

Table 5-2. Target concentrations for spiked metals in flue gas at TEAD.

Element	Low (ug/L)	Medium (ug/L)	High (ug/L)
Cd	70	100	500
Cr	5	50	200
Hg	100	500	1000
Ni	200	500	1000
Pb	10	25	50

5.4   FIELD TESTING AND SAMPLING PROTOCOL

Testing at both NADEP and TEAD consisted of Reference Method sampling where a time-integrated sample is collected on filter papers, impingers, and solutions submitted for off-site laboratory analyses, as well as ABF LIPS testing performed in real time. The reference methods are described in detail below. ABF LIPS measurements were made by fixed probe measurements (probe in center of duct) and spectra were collected every several minutes and processed manually after the field test.

5.4.1   NADEP

Test dates and a description of each run are shown in Table 5-1. Sampling details and other methodologies are described in the following subsections.

5.4.1.1 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.

5.4.1.1.1 Total Chromium Reference Method Sampling

Total chromium was measured using EPA Method 306 (the 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 ⅜" 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 C, 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 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.

5.4.1.1.2 Multiple Metals Reference Method Sampling

Multiple metals were measured by using EPA Method 29 (the reference method). 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 ⅜" 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 C, which also includes the calculation sheets. Volumetric flow rates of the exhaust duct were calculated from the measured velocity head and the cross-sectional area of the duct. As each traverse point was sampled, the velocity head of the flue gas was measured with an S-type Pitot tube connected to an inclined oil manometer, and the temperature of the flue gas was measured with a chromel-alumel (type K) thermocouple and a digital potentiometer (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 C.

5.4.2 TEAD

5.4.2.1 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 5-7 shows the platform just downstream from the afterburner that was used to support the spiking equipment.

Figure 5-7. 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 ± 20% target range, the system was considered to have reached a steady-state condition and the ABF-LIPS and reference method sampling commenced.

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 5-2. 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.

ABF-LIPS was set up on the platform of immediately upstream of the baghouse inlet, and the reference method equipment was located on the platform immediately downstream of the afterburner. 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 5-7 through 5-11.

Figure 5-8. 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 5-9. 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 5-10. ABF-LIPS instrument (cube structure at left) and laptop used for control and data storage at TEAD during September 2005 test.

Figure 5-11. 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.

5.4.2.2 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^oF. 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 C, which also includes the calculation sheets. Volumetric flow rates of the exhaust duct were calculated from the measured velocity head and the cross-sectional area of the duct. As each traverse point was sampled, the velocity head of the flue gas was measured with an S-type Pitot tube connected to an inclined oil manometer, and the temperature of the flue gas was measured with a chromel-alumel (type K) thermocouple and a digital potentiometer (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 C.

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.

5.5 SAMPLING PROTOCOL

Testing at NADEP consisted of three locations (sources): a chrome plating exhaust stack, an electroless nickel vent stack, and a Kirksite furnace exhaust stack. Each source was tested by injecting an aerosol of dissolved target metals as previously described at each of three concentrations. In addition, a baseline sample was collected at the nickel and Kirksite locations, where no metals were spiked. A number of the test runs were aborted due to various technical problems including clogging of the metals spiking orifice, broken probes, and power failures. The completed test runs, with dates, are shown in Table 5-3.

Table 5-3. Test runs at NADEP at various metals spike concentrations (Low, Medium, High; Baseline = no spiking).

1. Date\Run Number	2. 1 3.	2	4. 3	5. 4	6. Location
7. June 16, 2003	8. M	9.	10.	11.	12. Cr site
13. June 17, 2003	14. M	15. H	16.	17.	18. Cr site
19. June 18, 2003	20. Baseline	21. L	22. M	23. H	24. Ni Bath
25. June 19, 2003	26. Baseline	27. L	28.	29.	30. Kirksite
31. June 20, 2003	32. M	33. H	34.	35.	36. Kirksite

Testing at TEAD consisted of a single location. The first field test at TEAD during October 2004 was aborted due to inclement weather. The second TEAD test was performed during September 13-15, 2005. Table 5-4 describes the test runs and dates at TEAD's munitions deactivation furnace (APE 1232M).

Table 5-4. Test runs at TEAD.

Date	Run ID	Spike Concentration
September 13, 2005	TAD-1, TAD-2, TAD-3, TAD-4	Low
September 14, 2005	TAD-5, TAD-6, TAD-7, TAD-8	Medium
September 14, 2005	TAD-9	High
September 15, 2005	TAD-10, TAD-11, TAD-12	High

5.6 SAMPLING RESULTS

5.6.1 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 D.

5.6.1.1   Chromium Plating Reference Method Source Test

Table 5-5 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. Results are shown graphically in Figure 5-12 (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.

Table 5-5. Reference method results by EPA Method 306 for chromium plating exhaust, NADEP 2003.

Test Number:	1	2	3
Sampling Date:	6/16/03	6/17/03	6/17/03
Sample Number:	472-1	472-3	472-5
Spiking:	None	Medium	High
Flue Gas			
Temperature, ^{o}F	71	72	73
Velocity, ft/sec	42.4	42.5	42.5
Static Pressure, in. of H_2O	-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
Total Chromium			
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
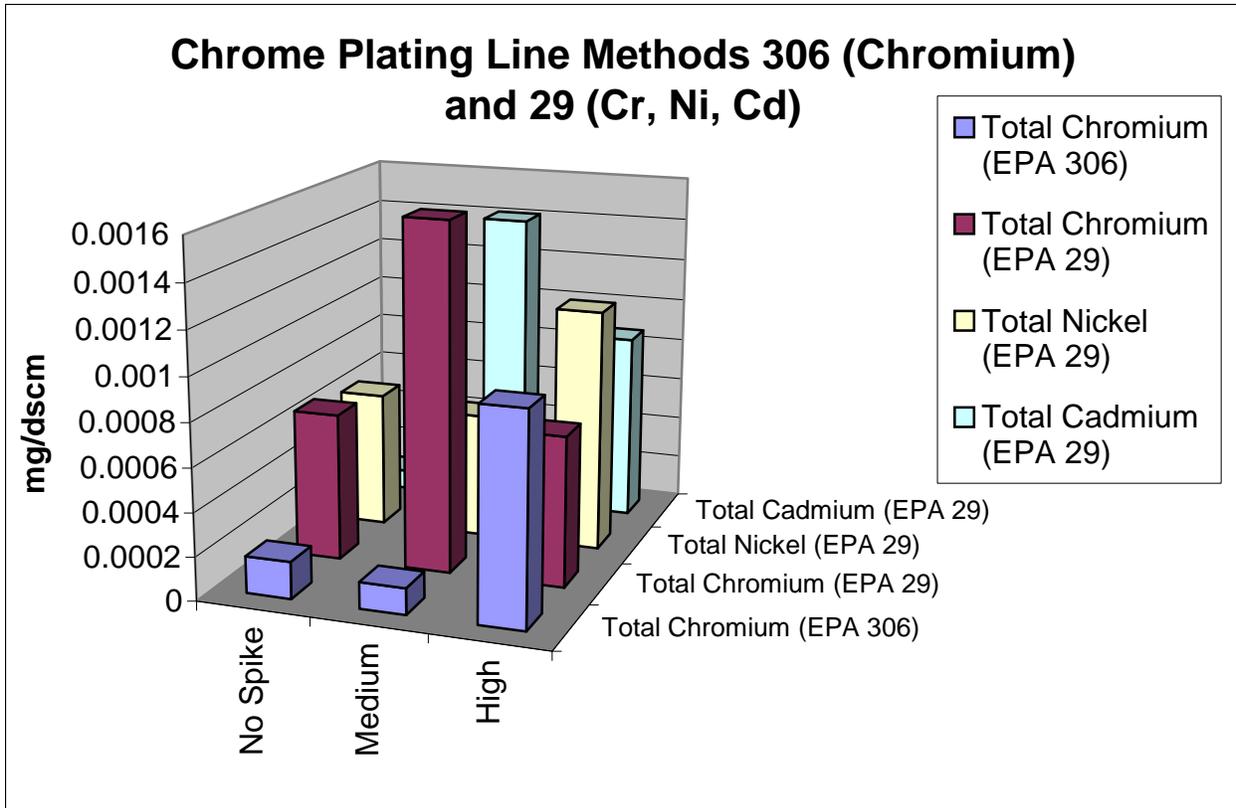
Figure 5-12. Comparison of results of reference method testing using two different methods (EPA Methods 306 and 29) simultaneously for chromium showing disparity of results (two front-most rows). Nickel and cadmium results from Method 29 are also shown. Chrome plating bath exhaust at NADEP, 2003.

Table 5-6 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 5-12. 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.

Table 5-6. Reference method results by EPA Method 29 for chromium plating exhaust, NADEP 2003.

Test Number:	1	2	3
Sampling Date:	6/16/03	6/17/03	6/17/03
Sample Number:	472-2	472-4	472-6
Spiking:	None	Medium	High
Flue Gas			
Temperature, °F	69	72	72
Velocity, ft/sec	43.5	43.4	43.9
Static Pressure, in. of H_2O	-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
Metals			
Sample Start	16:49	09:58	13:56
Sample Stop	18:55	12:05	16:02
Sampling Time, min.	120	120	120
Sample Volume, DSCF	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.

5.6.1.2 Nickel Plating Bath Exhaust Reference Method Source Test

Table 5-7 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 5-13. 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, 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.

Table 5-7. Reference method results for nickel plating exhaust, NADEP 2003.

Test Number:	1	2	3	4
Sampling Date:	6/18/03	6/18/03	6/18/03	6/18/03
Sample Number:	472-7	472-8	472-9	472-10
Spiking:	None	Low	Medium	High
Flue Gas				
Temperature, °F	78	78	78	79
Velocity, ft/sec	21.2	21.1	21.3	21.3
Static Pressure, in. of H_2O	-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
Metals				
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.
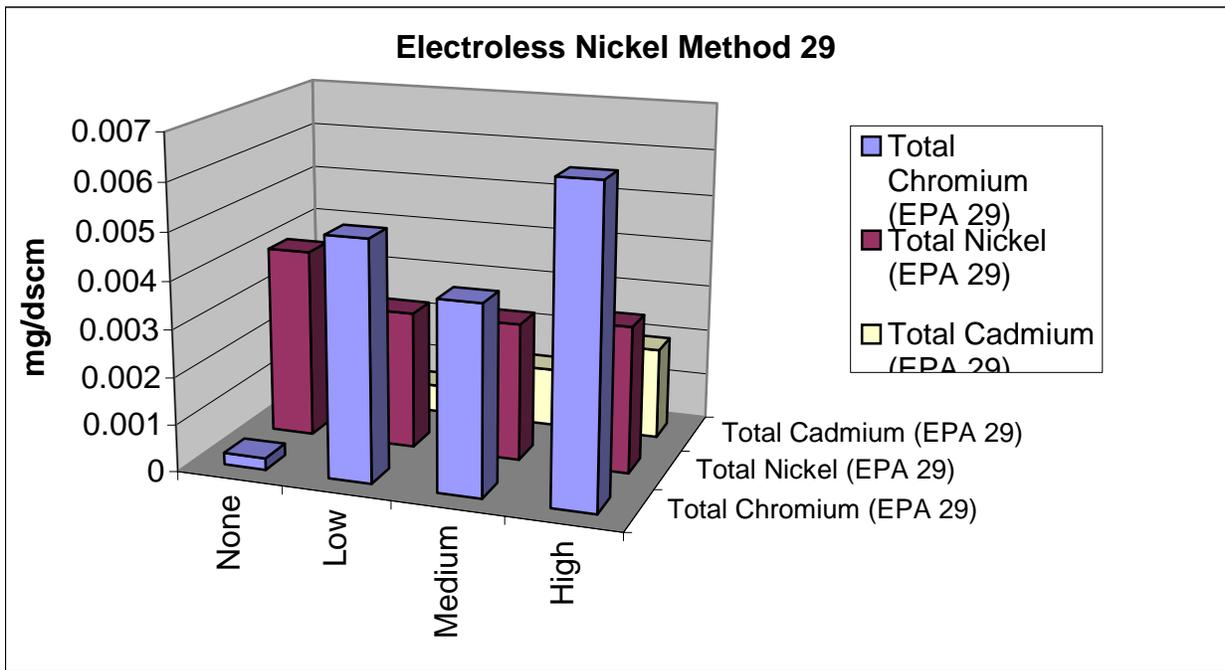
Figure 5-13. Electroless nickel plating bath exhaust stack Method 29 results during baseline (no spiking - none), and after spiking three concentrations of metals (low, medium, high).

5.6.1.3 Kirksite Furnace Exhaust Reference Method Source Test

Table 5-8 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 5-14.

Table 5-8. Reference method results for Kirksite furnace exhaust, NADEP 2003.

Test Number:	1	2	3	4
Sampling Date:	6/19/03	6/19/03	6/20/03	6/20/03
Sample Number:	65-1	65-2	65-3	65-4
Spiking:	None	Low	Medium	High
Flue Gas				
Temperature, °F	81	80	77	76
Velocity, ft/sec	43.5	43.6	42.9	43.5
Static Pressure, in. of H_2O	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
Metals				
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.
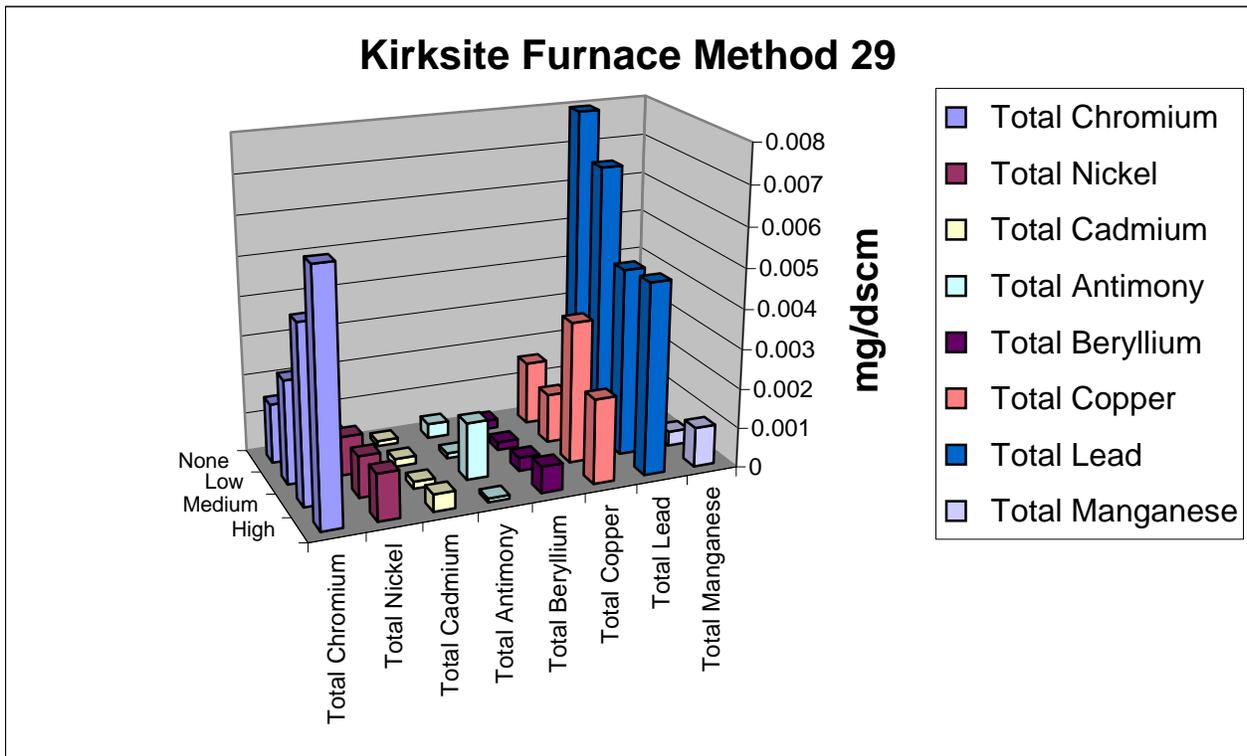
Figure 5-14. Reference method results for Kirksite furnace at NADEP.

5.6.1.4 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 5-9 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 5-10 presents the reference method results for the electroless nickel exhaust.

Table 5-9. 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.

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 5-10. Reference method results at electroless nickel plating bath exhaust stack, NADEP.

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

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 5-11, 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 calcuable standard deviation. Data are presented graphically in Figures 5-15 through 5-17.

Table 5-11. Chromium plating bath exhaust measurements using ABF-LIPS and reference method.

| Element	Measurment 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
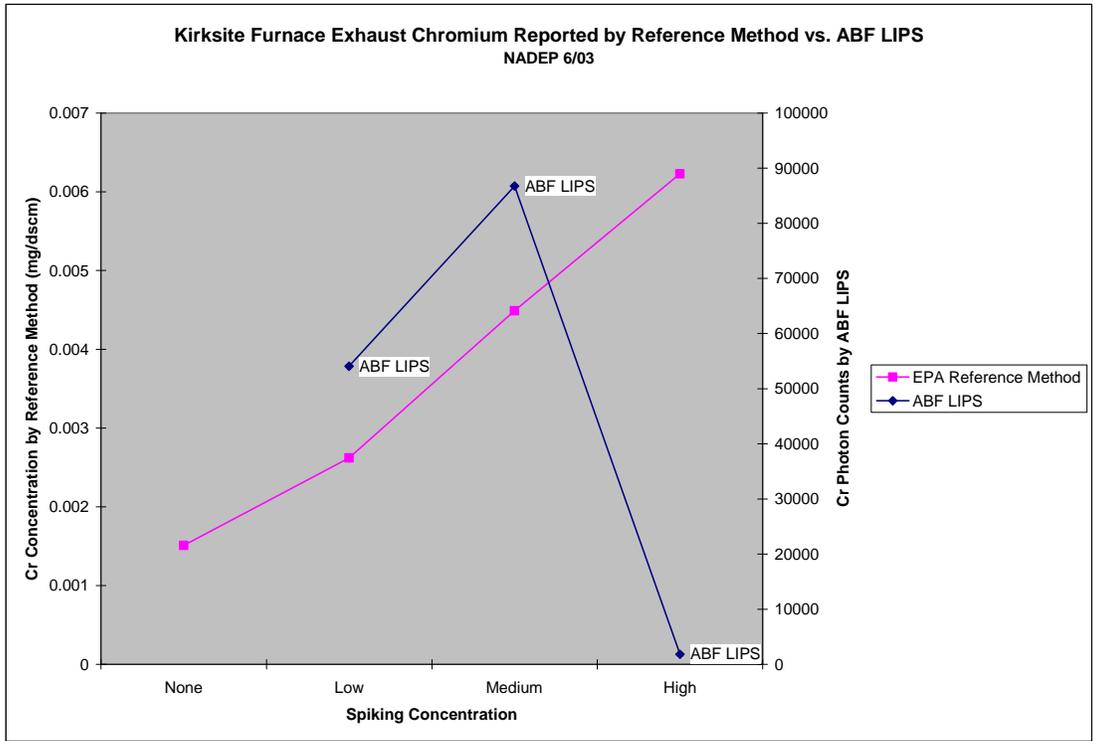
Figure 5-15. ABF-LIPS results vs. reference method for chromium at Kirksite furnace, NADEP.
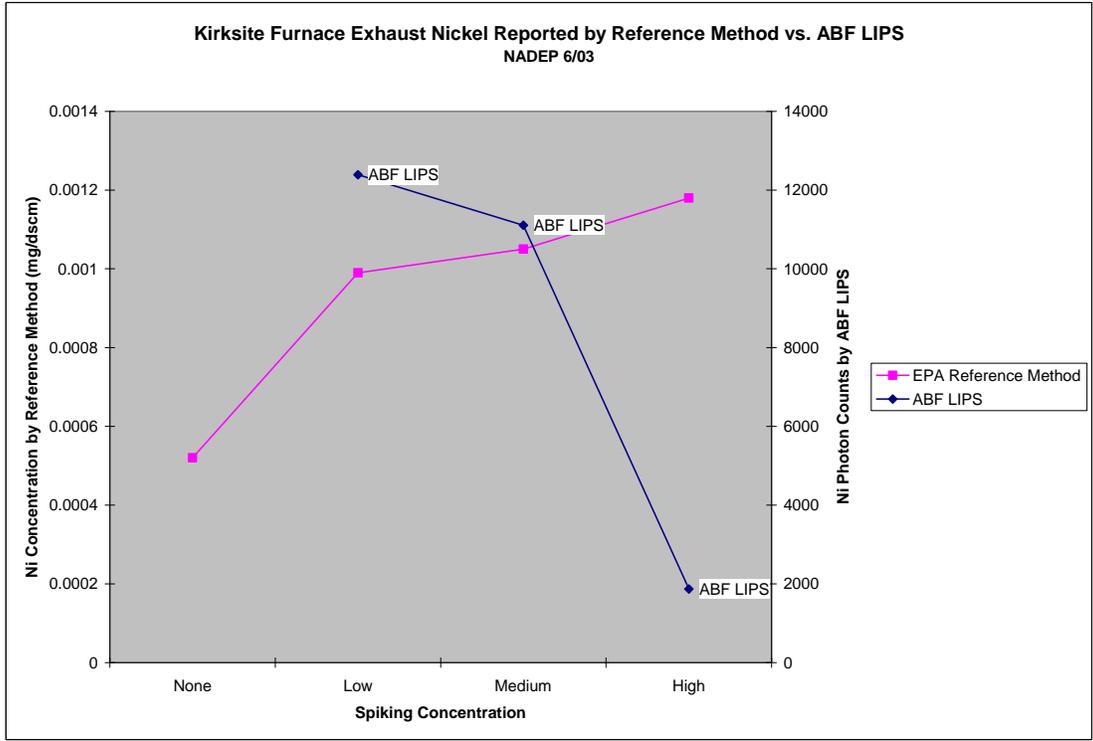

Figure 5-16. ABF-LIPS results vs. reference method for nickel at Kirksite furnace, NADEP.
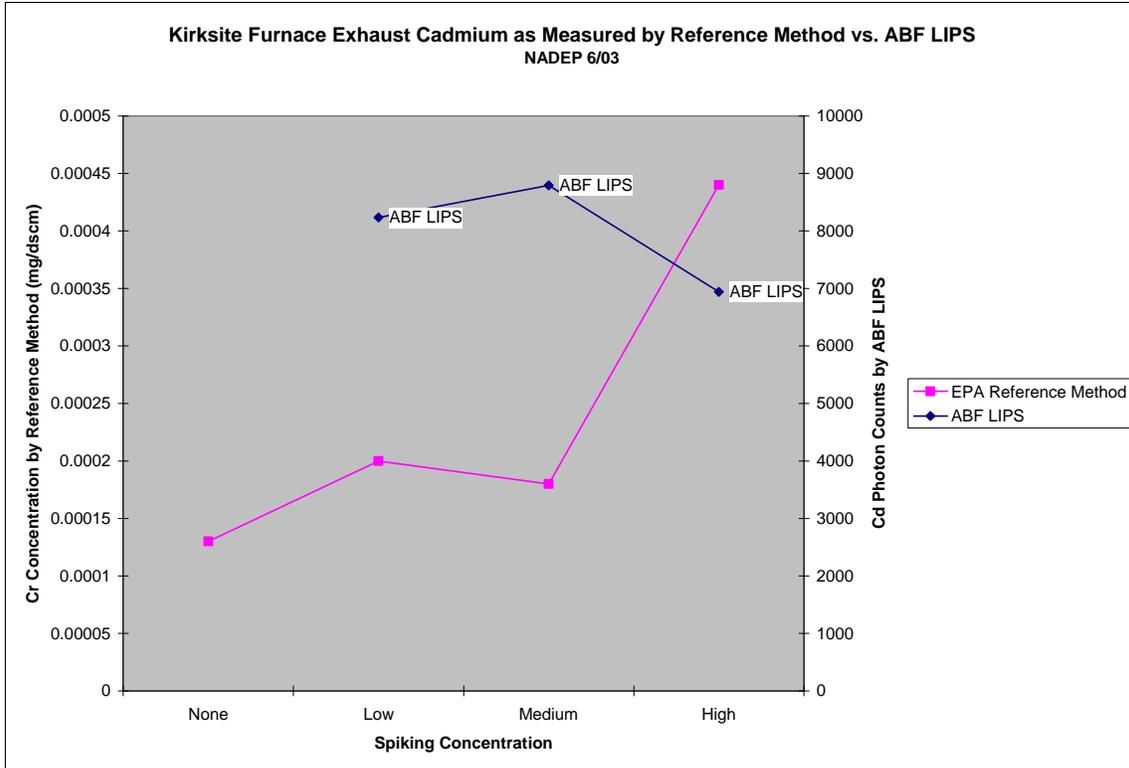
Figure 5-17. ABF-LIPS results vs. reference method for cadmium at Kirksite furnace, NADEP.

5.6.2 TEAD

5.6.2.1 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 5-12. Complete data from that run are included in Appendix C.

Table 5-12. Reference method result for low concentration spike run from October 2004 test at TEAD prior to canceling field test.

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

5.6.2.2   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). 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 5-13. The results include the average of the quadruplicate runs for both the reference method and ABF-LIPS, together with their standard deviation. Figures 5-18 through 5-22 present the data graphically.

Table 5-13. Results of September 2005 field test at TEAD comparing ABF-LIPS and reference method.

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
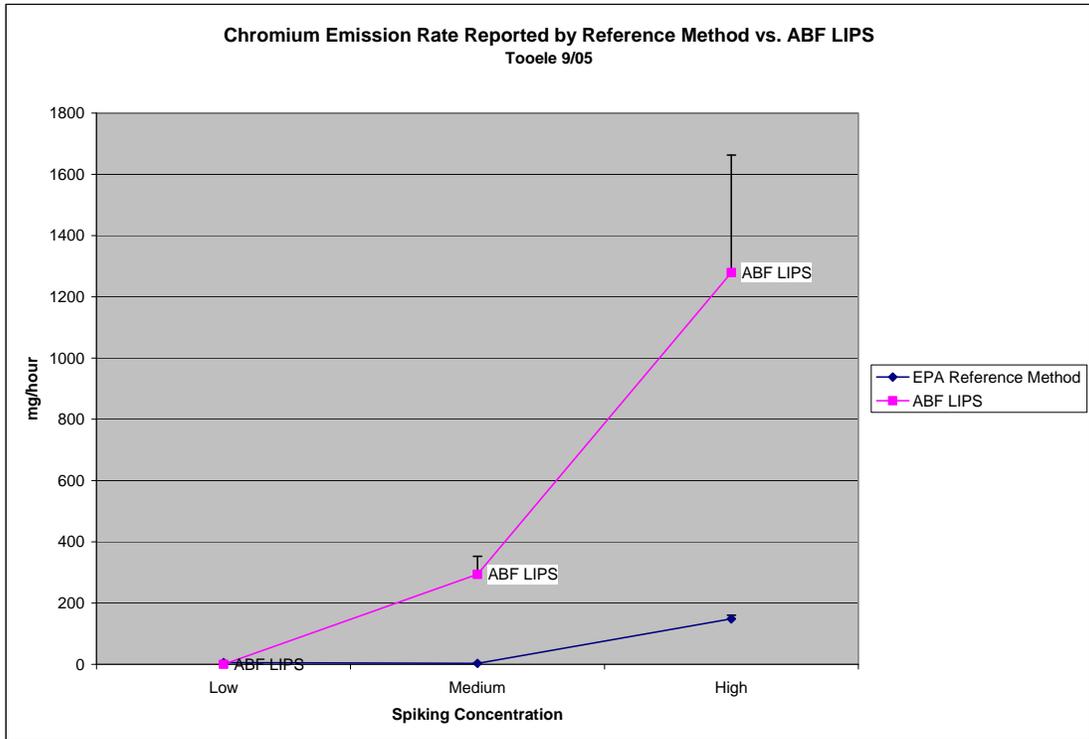
Figure 5-18. Chromium emission rates, with error bars (only positive half shown) as measured by ABF-LIPS and the reference method at TEAD.
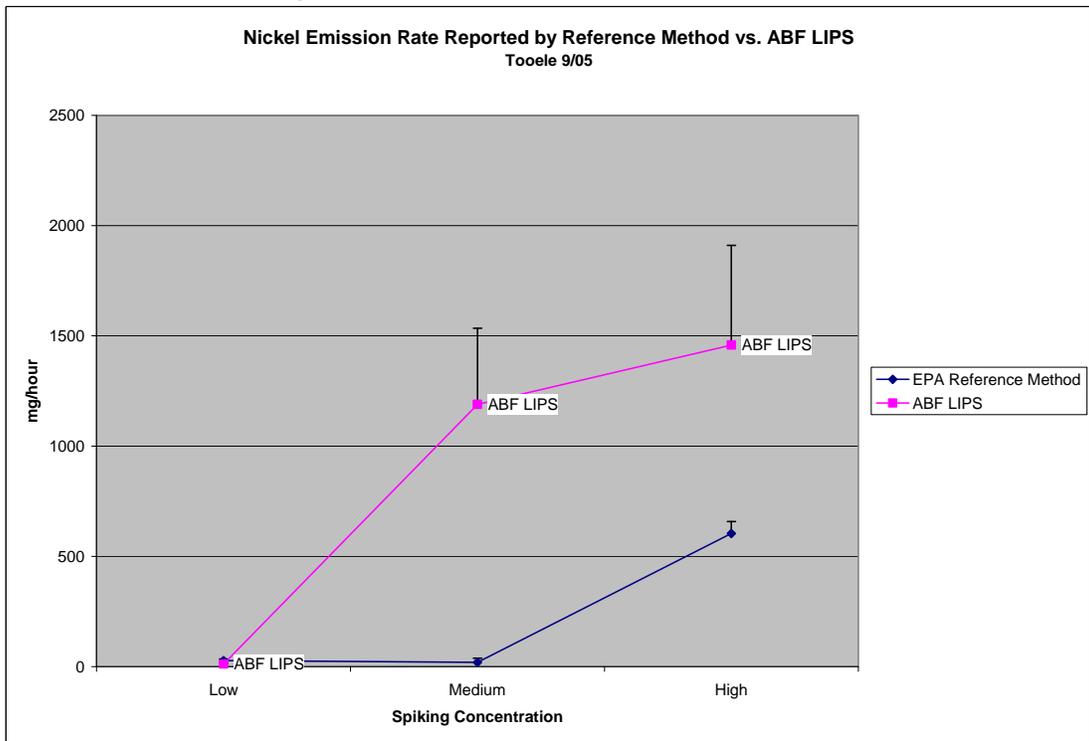
Figure 5-19. Nickel emission rates, with error bars (only positive half shown) as measured by ABF-LIPS and the reference method at TEAD.
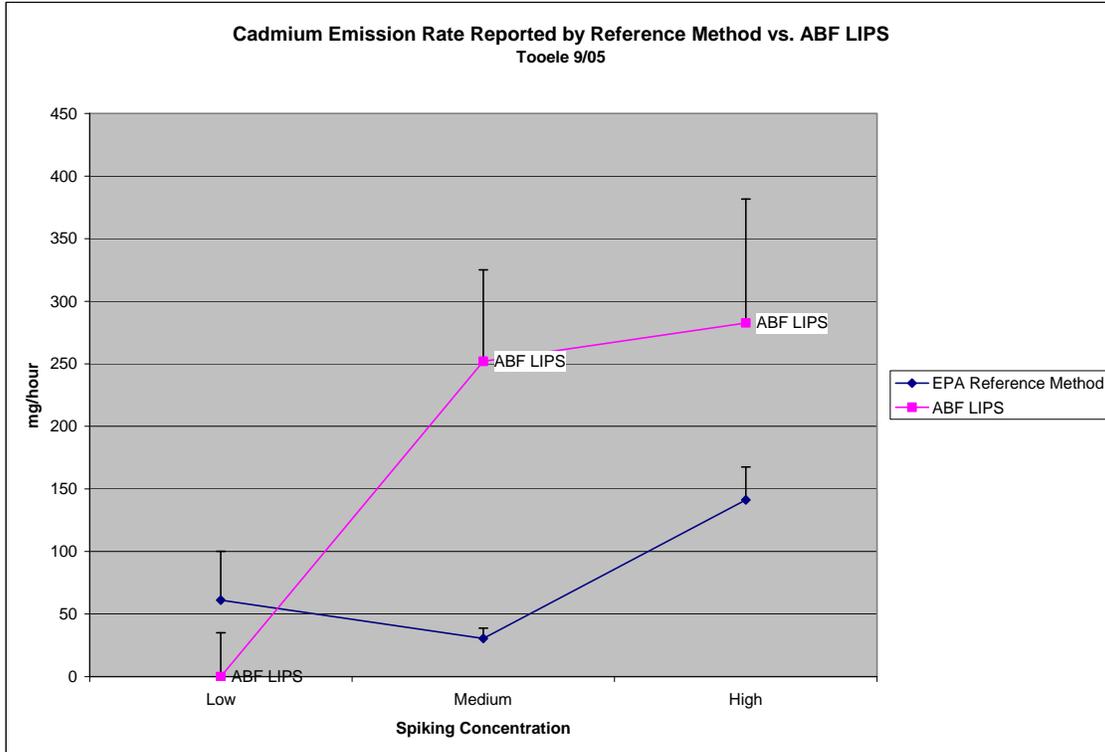
Figure 5-20. Cadmium emission rates, with error bars (only positive half shown) as measured by ABF-LIPS and the reference method at TEAD.
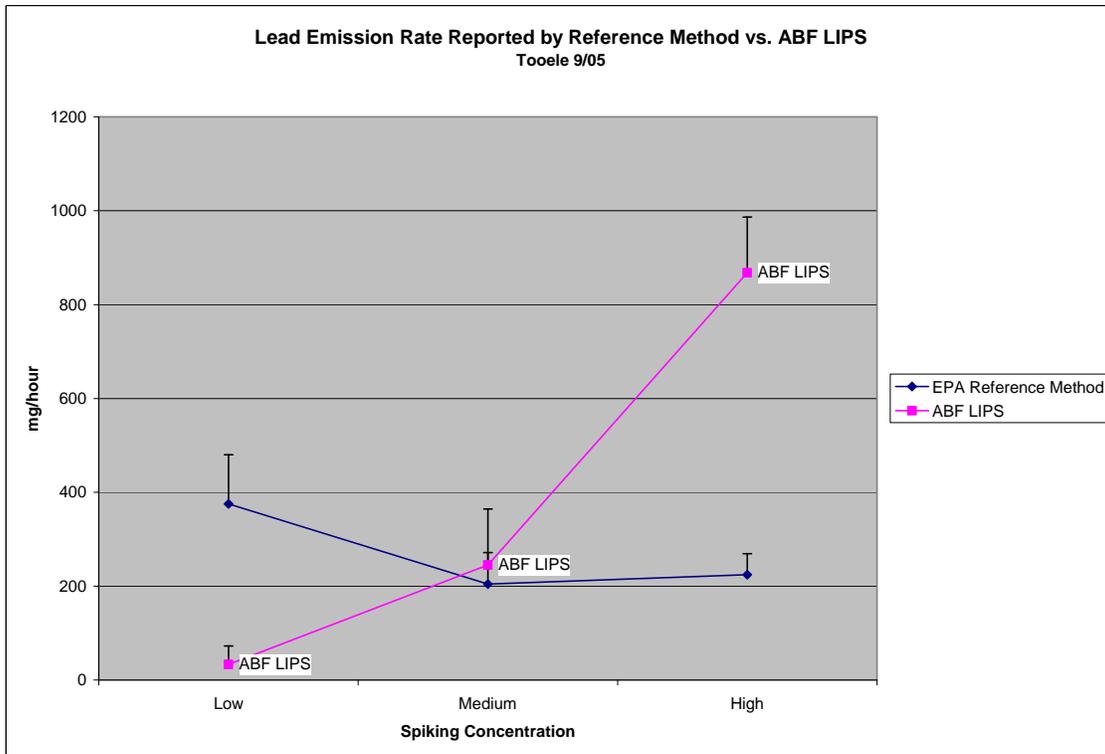

Figure 5-21. Lead emission rates, with error bars (only positive half shown) as measured by ABF-LIPS and the reference method at TEAD.
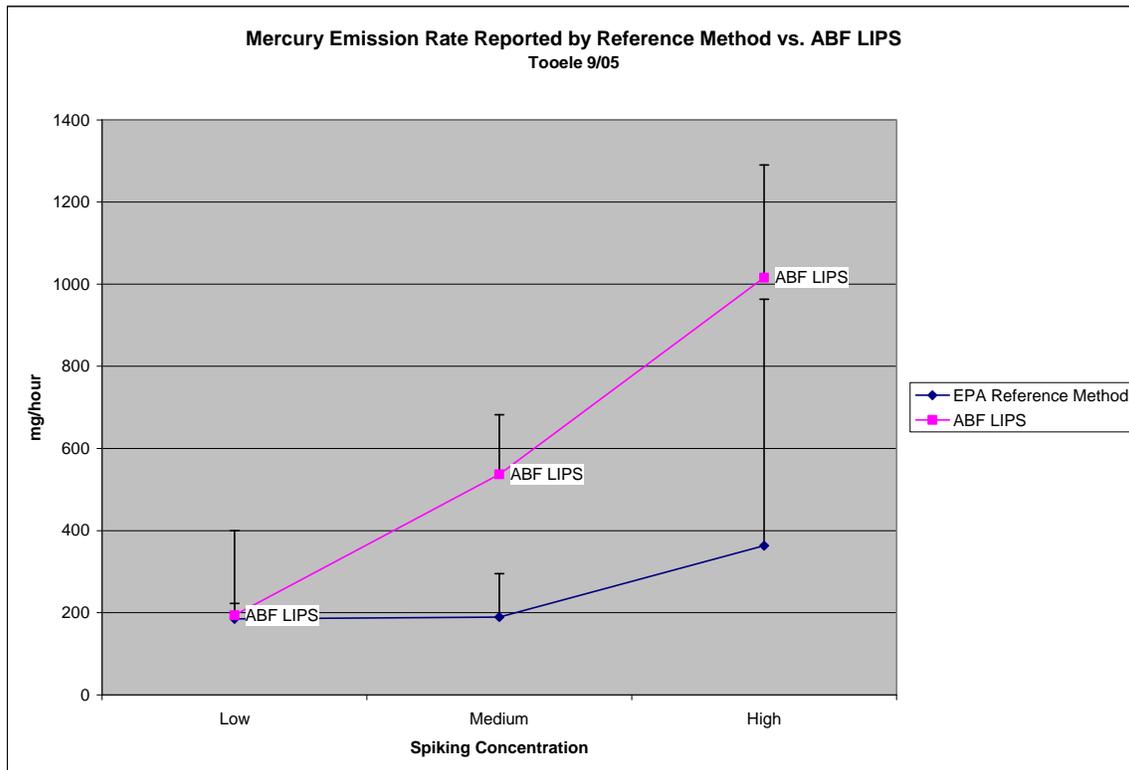
Figure 5-22. Mercury emission rates, with error bars (only positive half shown) as measured by ABF-LIPS and the reference method at TEAD.

5.7 PERFORMANCE CRITERIA

6 PERFORMANCE ASSESSMENT

Three field tests comprising four different sources were conducted. One field test at North Island Aviation Depot in San Diego was performed on three different sources in 2003. The following field test at Tooele Army Depot (TEAD) in Utah was aborted due to inclement weather but was repeated during 2005 with improvements to the instrument. The latter test at TEAD, while not meeting the primary performance objective of 20% for relative accuracy, was an improvement over the first field test at NADEP in terms of this primary performance criteria.

6.1 TECHNOLOGY COMPARISON

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 about 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 the 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 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.

6.2   PERFORMANCE CRITERIA

Performance Specification 10 (PS-10, included in Appendix B) specifies that multi-metals continuous emission monitoring systems.   Specifications from PS-10 pertinent to 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.

6.3 NADEP 2003 PERFORMANCE ASSESSMENT

ABF-LIPS field measurements for calibration (using the spike concentration corresponding to the first run and last run of each day), calibration drift, and zero drift were within the PS-10 requirements. Agreement with the reference method data, however, was poor, as indicated in the following subsections.

6.3.1 Chrome Plating Line and Electroless Nickel

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 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 6-1.

Table 6-1. Comparison of two reference methods for chromium.

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 to 29	-75.0	-92.5	39.1

6.3.2 Kirksite Furnace

Results from the Kirksite furnace show that ABF-LIPS measurements were not well correlated to the reference method. Best-fit lines through the data, with R^2 values are shown in Figures 6-1 through 6-3. R^2 values for the ABF-LIPS data are generally low compared to the reference method data, suggesting a random distribution in the ABF-LIPS results. As such, relative

accuracy for these data could not be calculated. An interim report for the NADEP results is included as Appendix D.
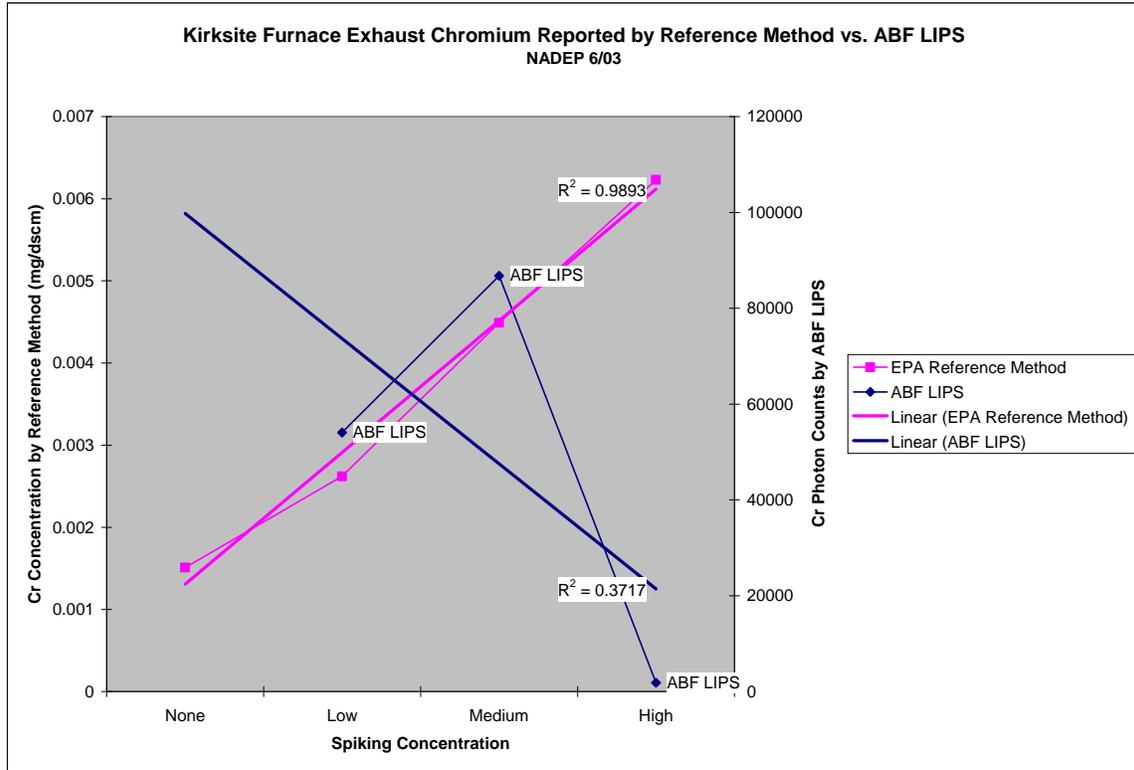
Figure 6-1. ABF-LIPS vs. reference method result for chromium at Kirksite furnace.
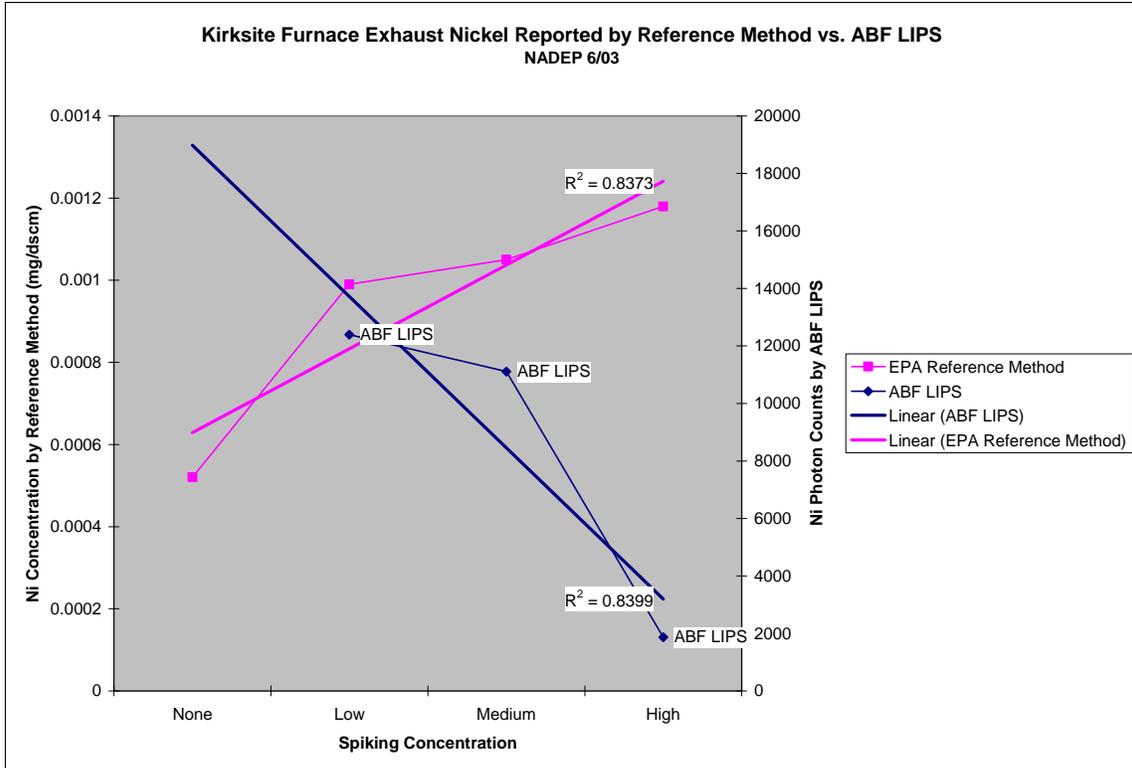
Figure 6-2. ABF-LIPS vs. reference method result for nickel at Kirksite furnace.
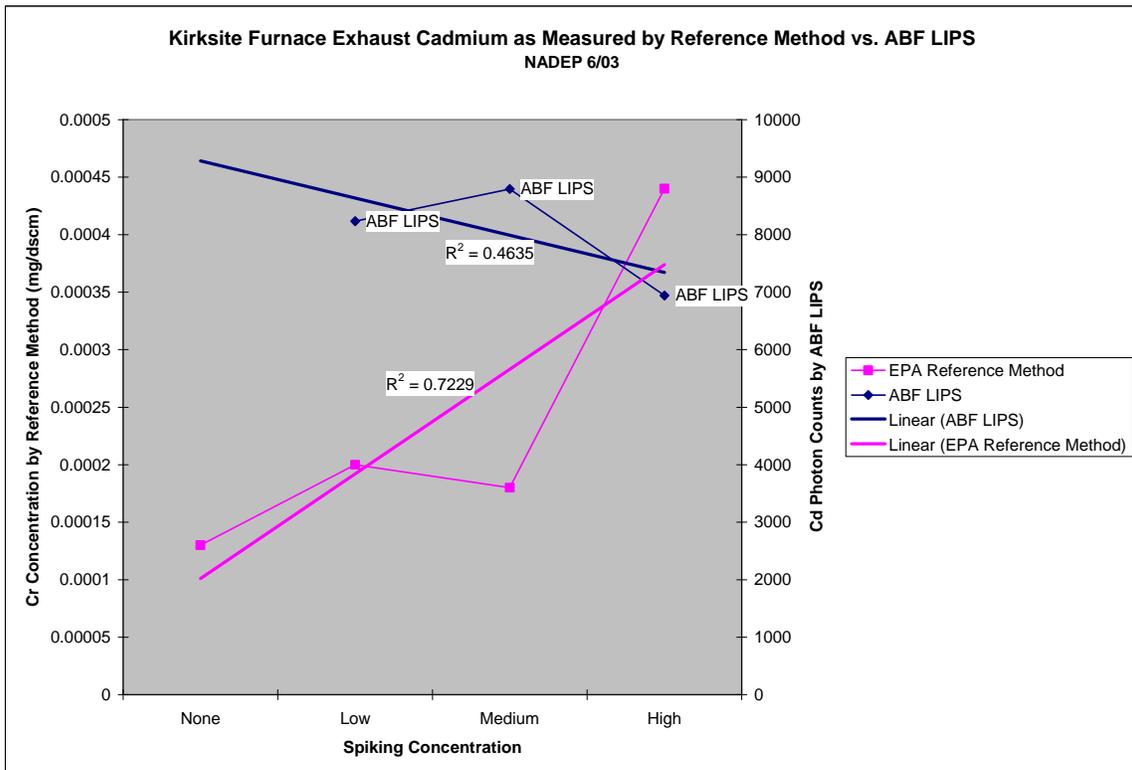
Figure 6-3. ABF-LIPS vs. reference method result for cadmium at Kirksite furnace.

6.4 TEAD 2005 PERFORMANCE ASSESSMENT

ABF-LIPS field measurements for calibration (using the spike concentration corresponding to the first run and last run of each day), calibration drift, and zero drift were within the PS-10 requirements. Agreement with the reference method data for relative accuracy, however, was generally poor.

The relative accuracy of ABF-LIPS to the reference method for the Tooele Army Depot September 2005 field test is presented in Table 6-2.

Table 6-2. Comparison of ABF-LIPS and reference method results from TEAD, September 2005.

		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%*

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 5-15. 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.

The data presented in Table 6-3 are shown graphically in Figures 6-4 through 6-7.
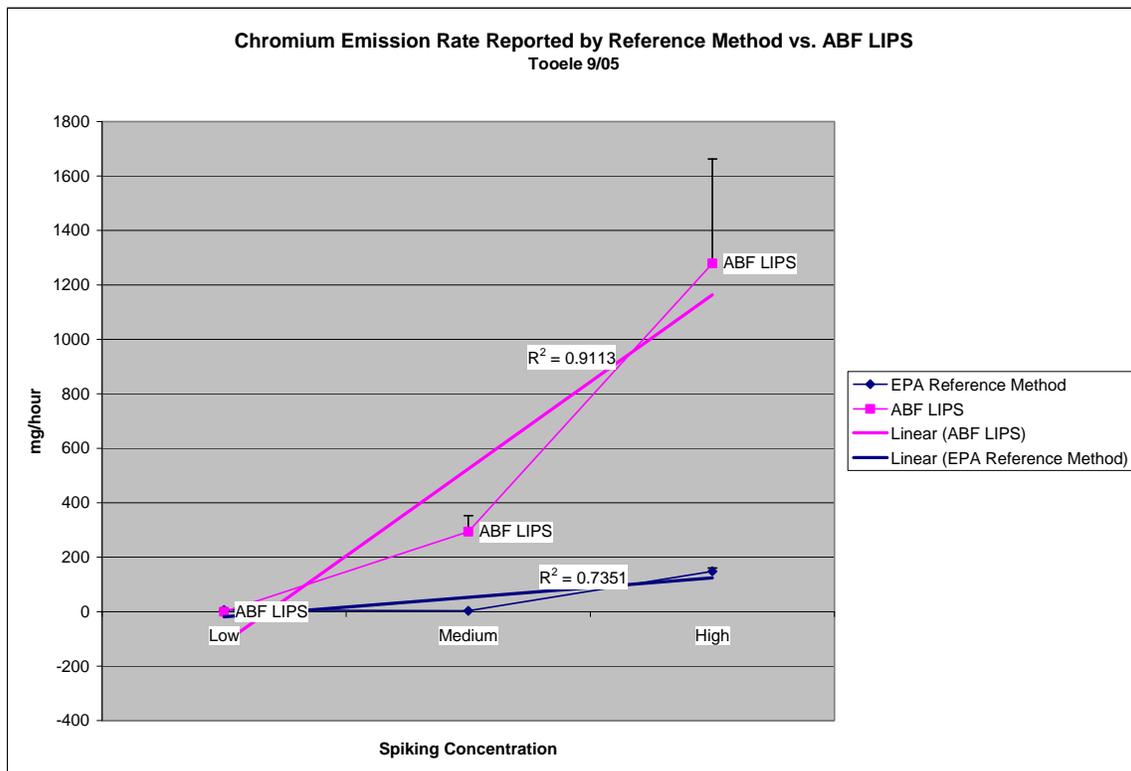
Figure 6-4. ABF-LIPS vs. reference method for chromium at Tooele Army Depot munitions deactivation furnace, September 2005.
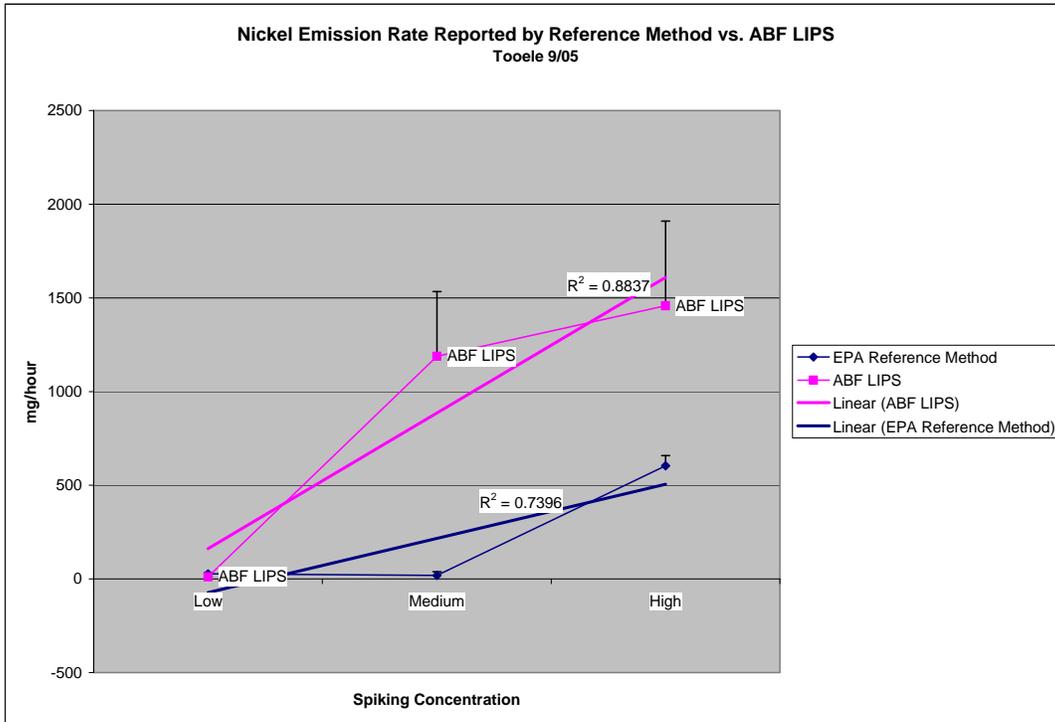
Figure 6-5. ABF-LIPS vs. reference method for nickel at Tooele Army Depot munitions deactivation furnace, September 2005.
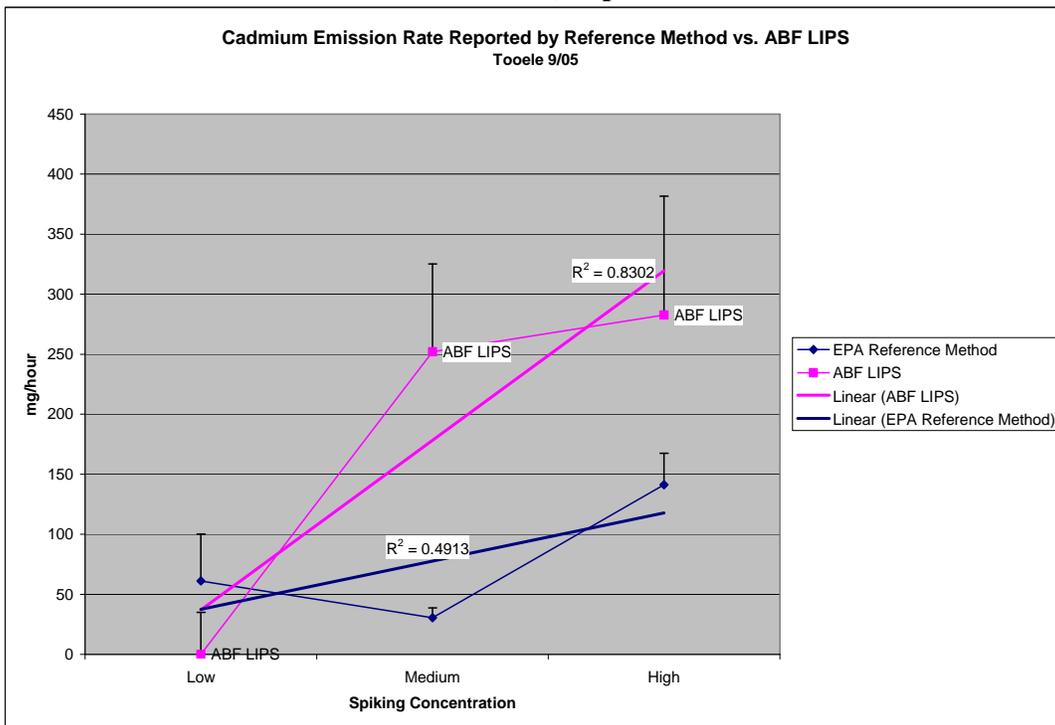

Figure 6-6. ABF-LIPS vs. reference method for nickel at Tooele Army Depot munitions deactivation furnace, September 2005.
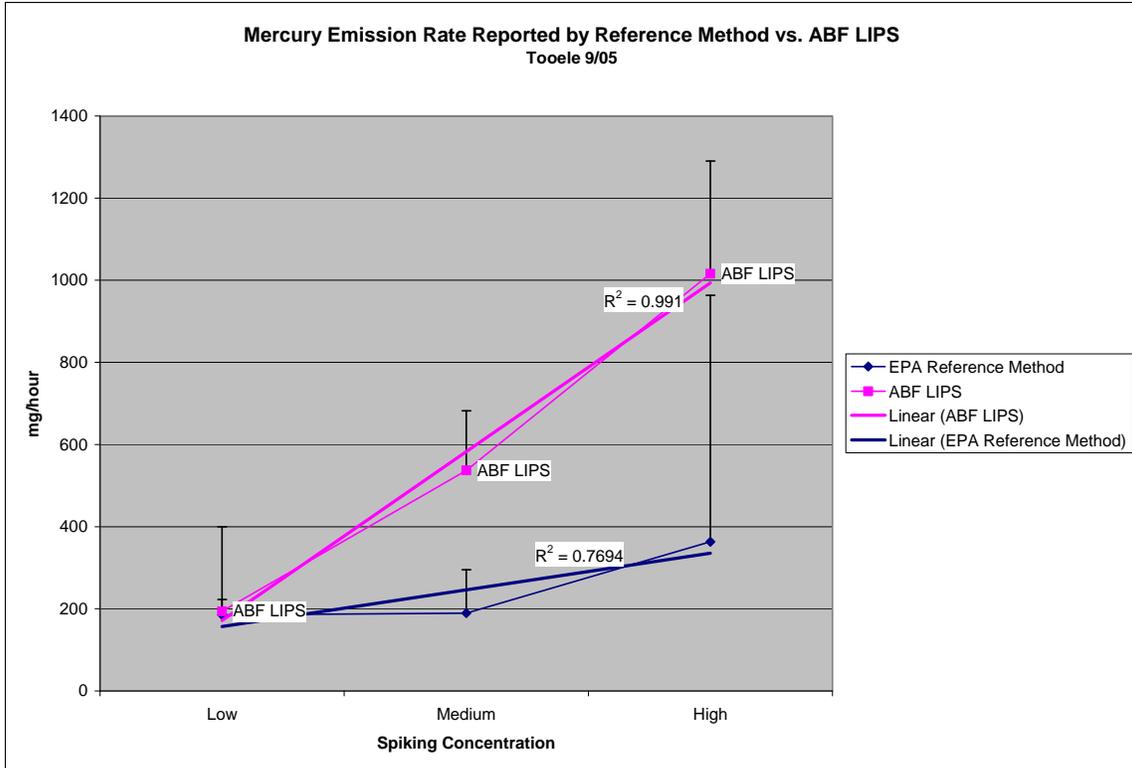
Figure 6-7. ABF-LIPS vs. reference method for mercury at Tooele Army Depot munitions deactivation furnace, September 2005.

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.

7   COST ASSESSMENT

7.1   COST MODEL

Since ABF LIPS uses very little consumables, and can be set for unattended operation, nearly all of the cost is in upfront site preparation, equipment purchase, and operator training. As such, no data was collected during the field tests which would significantly affect the cost of this technology. Estimates for ABF-LIPS capital and operating costs are listed in Table 7-1. Since these are rough estimates, a range of costs are given. Operating costs for ABF-LIPS are on an annual basis.

Table 7-1. Estimated cost of purchasing, installing, and beginning operation of ABF LIPS (single instrument).

Direct Environmental Activity Process Costs			
Start-Up		Operation & Maintenance	
Activity	$K	Activity	$K
Facility preparation, mobilization	10-250	Labor to operate equipment	10-20
Equipment design	5	Utilities	1-3
Equipment purchase	65-150	Consumables and supplies	1-2
Installation	20-40	Equipment maintenance	2-10
Training of operators	5-10	Training of operators	0

7.2   COST DRIVERS

Component costs include the high-power laser, the intensified charge couple array, and the spectrograph. The total for these three components is approximately $120,000, which provides wide-ranging capability in detecting metal-laden aerosols in near real-time. However, 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 $50,000 for four elements. The major saving by manufacturing a site-specific ABF-LIPS comes from the elimination of a detector costing $70,000 – 75,000 and replacement with a gateable photomultiplier tube plus a narrowband notch filter for an element. The aerosol sampling and focusing unit costs on the order of $7,000.   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.

Installation in remote locations in the outdoors, or on a tall stack would require construction of a weatherproof, ventilated climate-controlled housing. Depending on the site, these costs could exceed the purchase price of the instrument. Many sites, however, could benefit by installing ABF LIPS in buildings or on rooftops with little or no extra housing requirements.

7.3   COST ANALYSIS AND COMPARISON

Annual sampling of a stack source such as the furnace at Tooele costs $50k (subcontractor cost only) but does not require capital expenditures. A table showing cost estimates associated with ABF-LIPS and the current testing method, EPA Method 29, is shown below. Capital costs for an ABF-LIPS system capable of measuring multi-metals (all HAP metals) is $65-160k, and site preparation (including housing) are estimated to cost $35-295k, largely depending on the site characteristics such as availability of electricity, and the availability of a climate-controlled building to house the instrument. 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.   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.

Annual O&M costs for ABF-LIPS are projected to be $14-35k. Assuming the usuable life of an ABF-LIPS unit is 10 years, the annualized cost is $26k (annual O&M + $160k/10). Thus ABF-LIPS would save $14k/year, which does not consider the potential upcoming regulatory requirement of a CEMS coupled with the possible alternative of more frequent traditional sampling.

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 (*for comparison*)	5	Overhead assoc. with process (*for comparison*)	2
Equipment design	5	Utilities	1-3	Document maintenance (*for comparison*)	2	Productivity/Cycle time (*for comparison*)	0
Equipment purchase	65-160	Consumables and supplies	1-2	Envr. Mgmt. Plan development & maintenance (*for comparison*)	5	Worker injury claims & health costs (*for comparison*)	0
Installation	20-40	Equipment maintenance	2-10	Reporting requirements (*for comparison*)	3		
Training of operators	5-10	Training of operators	0	Test/analyze waste streams (*existing process only*)	40		

8   IMPLEMENTATION ISSUES

8.1   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.

8.2   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.

8.3   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. Some matrix interference may be severe enough to limit the detection level to unacceptable levels. 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 detection levels.

Lastly, 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.

8.4 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.

8.5 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 (Dp > 10 µm) may not be collected effectively by the sampling nozzle, while small particles (Dp < 50 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 can be overcome by making adjustments to the analysis software or may require hardware modifications.

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 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.

8.6   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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APPENDIX B

PERFORMANCE SPECIFICATION 10 (PS-10)
Specifications and test procedures for multimetals continuous monitoring systems in stationary sources

PERFORMANCE SPECIFICATIONS FOR MULTI-METALS CEMS

B-1   APPLICABILITY AND PRINCIPLE

B-1.1 Applicability.   This specification is to be used for evaluating the acceptability of multi-metals continuous emission monitoring systems (CEMS) at the time of or soon after installation and whenever specified in the regulations. The CEMS may include, for certain stationary sources, a) a diluent (O) monitor (which must meet its own performance specifications: 40 CFR part 60, Appendix B, Performance Specification 3), b) flow monitoring equipment to allow measurement of the dry volume of stack effluent sampled, and c) an automatic sampling system. A multi-metals CEMS must be capable of measuring the total concentrations (regardless of specification) of two or more of the following metals in both their vapor and solid forms: Antimony (Sb), Arsenic (As), Barium (Ba), Beryllium (Be), Cadmium (Cd), Chromium (Cr), Lead (Pb), Mercury (Hg), Silver (Ag), Thallium (Tl), Manganese (Mn), Cobalt (Co), Nickel (Ni), and Selenium (Se). Additional metals may be added to this list at a later date by addition of appendices to this performance specification. If a CEMS does not measure a particular metal or fails to meet the performance specifications for a particular metal, then the CEMS may not be used to determine emission compliance with the applicable regulation for that metal.
This specification is not designed to evaluate the installed CEMS' performance over an extended period of time nor does it identify specific calibration techniques and auxiliary procedures to assess the CEMS' performance. The source owner or operator, however, is responsible to properly calibrate, maintain, and operate the CEMS. To evaluate the CEMS' performance, the Administrator may require, under Section 114 of the Act, the operator to conduct CEMS performance evaluations at other times besides the initial test. See Sec. 60.13 (c) and "Quality Assurance Requirements for Multi-Metals Continuous Emission Monitoring Systems Used For Compliance Determination."

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

B-2 DEFINITI   ONS

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

B-3. INSTALLATION AND MEASUREMENT LOCATION SPECIFICATIONS

B-3.1 The   CEMS Installation and measurement location. Install the CEMS at an accessible location downstream of all pollution control equipment where the metals concentrations measurements are directly representative or can be corrected so as to be representative of the total emissions from the affected facility. Then select representative measurement points or paths for monitoring in locations that the CEMS will pass the RA test (see Section B-7). If the cause of failure to meet the RA test is determined to be the measurement location and a satisfactory correction technique cannot be established, the Administrator may require the CEMS to be relocated. Measurement locations and points or paths that are most likely to provide data that will meet the RA requirements are listed below.

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

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

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

B-3.2   Reference Method (RM) Measurement Location and Traverse Points. The RM measurement location should be (1) at least eight equivalent diameters downstream of the nearest control device, point of pollutant generation, bend, or other point at which a change of pollutant concentration or flow disturbance may occur and (2) at least two equivalent diameters upstream from the effluent exhaust. The RM and CEMS locations need not be the same, however the difference may contribute to failure of the CEMS to pass the RA test, thus they should be as close as possible without causing interference with one another. The equivalent duct diameter is

calculated as per 40 CFR part 60, Appendix A, Method 1, Section 2.1. Selection of traverse measurement point locations should be made according to 40 CFR part 60, Appendix A, Method 1, Sections 2.2 and 2.3. If the RM traverse line interferes with or is interfered by the CEMS measurements, the line may be displaced up to 30 cm (or 5 percent of the equivalent diameter of the cross section, whichever is less) from the centroidal area.

B-4   PERFORMANCE AND EQUIPMENT SPECIFICATIONS

B-4.1   Data Recorder Scale. The CEMS data recorder response range must include zero and a high level value. The high level value must be equal to the span value. If a lower high level value is used, the CEMS must have the capability of providing multiple outputs with different high level values (one of which is equal to the span value) or be capable of automatically changing the high level value as required (up to the span value) such that the measured value does not exceed 95 percent of the high level value.

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

B-4.3 Calibration   Drift. The CEMS design must allow the determination of calibration drift at concentration levels commensurate with the applicable emission standard for each metal monitored. The CEMS calibration may not drift or deviate from the reference value (RV) of the calibration standard used for each metal by more than 5 percent of the emission standard for each metal. The calibration shall be performed at a point equal to 80 to 120 percent of the applicable emission standard for each metal. 4.4 Zero Drift. The CEMS design must allow the determination of calibration drift at the zero level (zero drift) for each metal. If this is not possible or practicable, the design must allow the zero drift determination to be made at a low level value (zero to 20 percent of the emission limit value). The CEMS zero point for each metal shall not drift by more than 5 percent of the emission standard for that metal.

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

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

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

B-4.5.3   <u>Response Time for Batch CEMS</u>. The response time requirement of Section B-4.5.1 and B-4.5.2 do not apply to batch CEMS. Instead it is required that the sampling time be no longer than one third of the averaging period for the applicable standard. In addition, the delay

between the end of the sampling period and reporting of the sample analysis shall be no greater than one hour. Sampling is also required to be continuous except in that the pause in sampling when the sample collection media are changed should be no greater than five percent of the averaging period or five minutes, whichever is less.

B-5   PERFORMANCE SPECIFICATION TEST PROCEDURE

B-5.1 Pretest   Preparation. Install the CEMS and prepare the RM test site according to the specifications in Section B-3, and prepare the CEMS for operation according to the manufacturer's written instructions.

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

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

B-6.0   THE CEMS CALIBRATION AND ZERO DRIFT PROCEDURE

This performance specification is designed to allow calibration of the CEMS by use of standard solutions, filters, etc that challenge the pollutant analyzer part of the CEMS (and as much of the whole system as possible), but which do not challenge the entire CEMS, including the sampling interface. Satisfactory response of the entire system is covered by the RA requirements. The CD measurement is to verify the ability of the CEMS to conform to the established CEMS calibration used for determining the emission concentration. Therefore, if periodic automatic or manual adjustments are made to the CEMS zero and calibration settings, conduct the CD test immediately before the adjustments, or conduct it in such a way that the CD and ZD can be determined. Conduct the CD and ZD tests at the points specified in Sections B-4.3 and B-4.4. Record the CEMS response and calculate the CD according to:

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

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

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

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

B-7   RELATIVE ACCURACY TEST PROCEDURE

B-7.1   Sampling Strategy for RA Tests. The RA tests are to verify the initial performance of the entire CEMS system, including the sampling interface, by comparison to RM measurements. Conduct the RM measurements in such a way that they will yield results representative of the emissions from the source and can be correlated to the CEMS data. Although, it is preferable to conduct the diluent (if applicable), moisture (if needed), and pollutant measurements simultaneouly, the diluent and moisture measurements that are taken within a 30- to 60-minute period, which includes the pollutant measurements, may be used to calculate dry pollutant concentration.

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

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

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

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

B-7.4 Reference   Methods. Unless otherwise specified in an applicable subpart of the regulations, Method 3B, or its approved alternative, is the reference method for diluent (O_2) concentration. Unless otherwise specified in an applicable subpart of the regulations, the manual method for multi-metals in 40 CFR part 266, Appendix IX, Section 3.1 (until superseded by SW-846), or its approved alternative, is the reference method for multi-metals.
As of 3/22/95 there is no approved alternative RM (for example, a second metals CEMS, calibrated absolutely according to the alternate procedure to be specified in an appendix to this performance specification to be added when an absolute system calibration procedure becomes available and is approved) to Method 29.

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

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

B-8 EQUATIO NS

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

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

where n is equal to the number of data points. 8.1.1 Calculate the arithmetic mean of the difference, d, of a data set, using Equation 3 and substituting d for x. Then

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

where x and y are paired data points from the CEMS and RM, respectively. 8.2 Standard Deviation. Calculate the standard deviation (SD) of a data set as follows:

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

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

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

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

Table B-1
t-Values

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

[a] The values in this table are already corrected for n-1 degrees of freedom. Use n equal to the number of individual values.

B-9   REPORTING

At a minimum (check with the appropriate regional office, or State, or local agency for additional requirements, if any) summarize in tabular form the results of the CD tests and the RA tests or alternate RA procedure as appropriate. Include all data sheets, calculations, and records of CEMS response necessary to substantiate that the performance of the CEMS met the performance specifications. The CEMS measurements shall be reported to the agency in units of $\mu g/m_3$ on a dry basis, corrected to 20°C or 7 percent O_2.

B-10 ALTERNATIVE   PROCEDURES

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

B-11 BIBLIOGRAPHY

1. 40 CFR part 60, Appendix B, "Performance Specification 2 - Specifications and Test Procedures for SO_x and NO_x Continuous Emission Monitoring Systems in Stationary Sources."
2. 40 CFR part 60, Appendix B, "Performance Specification 1 - Specification and Test Procedures for Opacity Continuous Emission Monitoring Systems in Stationary Sources."
3. 40 CFR part 60, Appendix A, "Method 1 - Sample and Velocity Traverses for Stationary Sources."
4. 40 CFR part 266, Appendix IX, Section 2, "Performance Specifications for Continuous Emission Monitoring Systems."
5. Draft Method 29, "Determination of Metals Emissions from Stationary Sources," Docket A-90-45, Item II-B-12, and EMTIC CTM-012.WPF.
6. "Continuous Emission Monitoring Technology Survey for Incinerators, Boilers, and Industrial Furnaces: Final Report for Metals CEM's," prepared for the Office of Solid Waste, U.S. EPA, Contract No. 68-D2-0164 (4/25/94).

APPENDIX C
Stack Sampling Field Notes

PES, Inc.	Metals Calculations						
Plant	Tooele Army Depot						
Project #	1111.001						
Operation	Burnoff Kiln						
Run	TAD-4						
Location	Baghouse Exhaust						
Date	10/26/2004						
INPUTS							
Vlc =	53.40	cc	Vol. Of H2O collected (impingers)				
Vm =	62.250	cf	Dry gas meter reading				
Pb =	24.80	in. Hg	Barometric pressure				
Ps =	24.78	in. Hg	Stack pressure				
dP^0.5 =	0.505		Average sq.rt delta P				
dH =	1.81	in. H2O	Average delta H reading				
Tm =	52.8	F	Average meter temperature				
Ts =	388.6	F	Average stack temperature				
Dn =	0.322	in.	Nozzle diameter				

Y =	1.007		Meter calibration factor			
t =	80	min.	Duration of sampling time			duct diameter (in):
A =	2.18	sq.ft.	Cross sectional area of stack	0.833	9.996339	
Cp =	0.84		Pitot tube coefficient			
Kp =	85.49		Pitot tube constant			
K1 =	17.64	R/in.Hg	constant			
K2 =	0.04707	cu.ft/ml	constant			
K3 =	0.002669	in.Hg-cf/ml-R	constant			
[O2] =	17	%	(Assumed)			
[CO2] =	3.0	%	N2 = 100 – (CO2 + O2)			
Tooele Army Depot		Baghouse Exhaust				
Run #	TAD-4					
Page 2						
CALCULATIONS						
1) Volume of gas sampled at standard conditions, Vmstd						
Vmstd =K1* Y * Vm *(Pb + dH/13.6)/Tm						
Vmstd =	53.77	cu.ft				
	1.52	cu.m				
2) Volume of water vapor collected at standard conditions.						
Vw(std) = K2 * Vlc						
Vw(std) =	2.51	scf				

3) Decimal fraction of moisture by volume in stack gas							
Bws = Vwstd/(Vmstd+Vwstd)							
Bws =	0.045						
4) Molecular weight of the stack gas on a wet basis Ms.							
Ms = (1-Bws)*((44*%CO2)+(32*%O2)+(28*%N2))+(18*Bws)							
Ms =	28.63						
5) Average stack gas velocity.							
Vs = Kp*Cp*(dP^0.5)*(Ts/(Ps*Ms))^0.5							
vs =	39.63	ft/sec					
6) Average actual stack gas volumetric flowrate.							
Q = 60 * vs * As							
Q =	5183	cfm					
	146.79	cmm					
Tooele Army Depot		Baghouse Exhaust					
Run #	TAD-4						
Page 3							
7) Average stack gas dry volumetric flowrate.				Tstd = 68oF			
Qstd = Q * (Tstd/Ts) * (Ps/Pstd)				Pstd = 29.92 in. Hg			

Qstd =	2552	dscfm					
	72.28	dscmm					
8) Analytical data							
Metals Concentrations							
Nickel							
C(Ni)1 =	0.0002	mg/l Concentration of Ni in charge blank					
V(1) =	0.133	l Volume of charge					
m(Ni)1 =	0.000027	mg Total Ni in charge blank					
C(Ni)2 =	0.0002	mg/l Concentration of Ni in wash blank					
V(2) =	0.162	l Volume of wash					
m(Ni)2 =	0.000032	mg Total Ni in wash blank					
m(Ni)3 =	0.00027	mg Total Ni in filter blank					
m(Ni)4 =	0.06800	mg Total Ni in sample					
m(Ni)5 =	0.00033	mg Total Ni in sample blank					
m(Ni)6 =	0.06767	mg Total Ni net					
[Ni] =	0.044440	mg/dscm (m(Ni)6/Vmstd)					
E =	192.73	mg/hr					
Tooele Army Depot		Baghouse Exhaust					
Run #	TAD-4						

Cadmium						
C(Cd)1 =	0.0002	mg/l Concentration of Cd in charge blank				
V(1) =	0.133	l Volume of charge				
m(Cd)1 =	0.000027	mg Total Cd in charge blank				
C(Cd)2 =	0.0002	mg/l Concentration of Cd in wash blank				
V(2) =	0.162	l Volume of wash				
m(Cd)2 =	0.000032	mg Total Cd in wash blank				
m(Cd)3 =	0.00003	mg Total Cd in filter blank				
m(Cd)4 =	0.03500	mg Total Cd in sample				
m(Cd)5 =	0.00009	mg Total Cd in sample blank				
m(Cd)6 =	0.03491	mg Total Cd net				
[Cd] =	0.022926	mg/dscm (m(Cd)6/Vmstd)				
E =	99.43	mg/hr				
Chromium						
C(Cr)1 =	0.001	mg/l Concentration of Cr in charge blank				
V(1) =	0.133	l Volume of charge				
m(Cr)1 =	0.000133	mg Total Cr in charge blank				
C(Cr)2 =	0.001	mg/l Concentration of Cr in wash blank				

V(2) =	0.162	l Volume of wash				
m(Cr)2 =	0.000162	mg Total Cr in wash blank				
m(Cr)3 =	0.00086	mg Total Cr in filter blank				
m(Cr)4 =	0.01500	mg Total Cr in sample				
m(Cr)5 =	0.00116	mg Total Cr in sample blank				
m(Cr)6 =	0.01385	mg Total Cr net				
[Cr] =	0.009092	mg/dscm (m(Cr)6/Vmstd)				
E =	39.43	mg/hr				
Tooele Army Depot		Baghouse Exhaust				
Run #	TAD-4					
Page 5						
Lead						
C(Pb)1 =	0.0002	mg/l Concentration of Pb in charge blank				
V(1) =	0.133	l Volume of charge				
m(Pb)1 =	0.000027	mg Total Pb in charge blank				
C(Pb)2 =	0.0002	mg/l Concentration of Pb in wash blank				
V(2) =	0.162	l Volume of wash				
m(Pb)2 =	0.000032	mg Total Pb in wash blank				
m(Pb)3 =	0.00013	mg Total Pb in filter blank				

m(Pb)4 =	0.00510	mg Total Pb in sample					
m(Pb)5 =	0.00019	mg Total Pb in sample blank					
m(Pb)6 =	0.00491	mg Total Pb net					
[Pb] =	0.003225	mg/dscm (m(Pb)6/Vmstd)					
E =	13.99	mg/hr					
Mercury							
C(Hg)1 =	0.000040	mg/l Concentration of Hg in HNO3/H2O2 charge blank					
V(1) =	0.133	l Volume of charge					
m(Hg)1 =	0.000005	mg Total Hg in charge blank					
C(Hg)2 =	0.000055	mg/l Concentration of Hg in HNO3 wash blank					
V(2) =	0.162	l Volume of wash					
m(Hg)2 =	0.000009	mg Total Hg in wash blank					
C(Hg)3 =	0.000014	mg/l Concentration of Hg in KMNO4 charge blank					
V(1) =	0.151	l Volume of charge					
m(Hg)3 =	0.000002	mg Total Hg in charge blank					
C(Hg)4 =	0.000023	mg/l Concentration of Hg in H2O wash blank					
V(2) =	0.087	l Volume of wash					
m(Hg)4 =	0.000002	mg Total Hg in wash blank					
Tooele Army Depot		Baghouse Exhaust					
Run #	TAD-4						
Page 6							

Mercury (cont'd)							
m(Hg)5 =	0.000010	mg Total Hg in filter blank					
m(Hg)6 =	0.04905	mg Total Hg in sample					
m(Hg)7 =	0.00003	mg Total Hg in sample blank					
m(Hg)8 =	0.04902	mg Total Hg net					
[Hg] =	0.032193	mg/dscm (m(Hg)8/Vmstd)					
E =	139.62	mg/hr					
9) Isokinecity							
An =	0.00057	ft^2	Area of nozzle orifice				
% I = 100*Ts*((K3*Vlc+(Vm*Y/Tm)(Pb+dH/13.6))/(60*t*Ps*vs*An)							
% I =	101.6						
Tooele Army Depot		Test Date	10/26/2004				
Baghouse Exhaust		Barometer	24.80	in.Hg			
		Run #	TAD-4				
		Static P	-0.21	in.H2O			
		Pitot Cp	0.84				
		Nozzle	0.322				
Sample	Delta-P	Stack Temp.	Delta H	Gas Meter Temp		(dP)^.5	velocity
Time	(in. H2O)	(Deg.F)	(in. H2O)	IN	OUT		ft/sec

B-1	0.20	392	1.40	47	46	0.447	35.19
2	0.25	399	1.80	49	45	0.500	39.51
3	0.27	403	1.90	50	46	0.520	41.15
4	0.27	398	1.90	52	46	0.520	41.03
5	0.28	396	2.00	53	46	0.529	41.74
6	0.26	383	1.80	54	47	0.510	39.91
7	0.30	374	2.10	56	48	0.548	42.65
8	0.30	364	2.10	56	48	0.548	42.39
9	0.24	377	1.70	56	49	0.490	38.21
10	0.20	376	1.40	56	50	0.447	34.86
A-1	0.27	373	1.90	53	50	0.520	40.43
2	0.27	397	1.90	55	53	0.520	41.01
3	0.30	395	2.10	57	52	0.548	43.18
4	0.30	395	2.10	57	52	0.548	43.18
5	0.30	395	2.10	59	52	0.548	43.18
6	0.25	392	1.80	60	53	0.500	39.35
7	0.25	391	1.80	60	53	0.500	39.32
8	0.23	390	1.60	61	54	0.480	37.70
9	0.20	393	1.40	62	54	0.447	35.21
10	0.18	388	1.30	59	54	0.424	33.31
		388.6	1.81	55.6	49.9	0.505	**39.63**
				Avg.	52.8		

APPENDIX D
ABF-LIPS Spectra Collected at NADEP Field Test, 2003

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

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

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

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

Fig. 13. Averaged spectrum of the baseline emissions at the Ni site. Major elements identified are also shown in the figure. No major peaks found beyond 600-nm wavelength, which region is excluded from the figure.
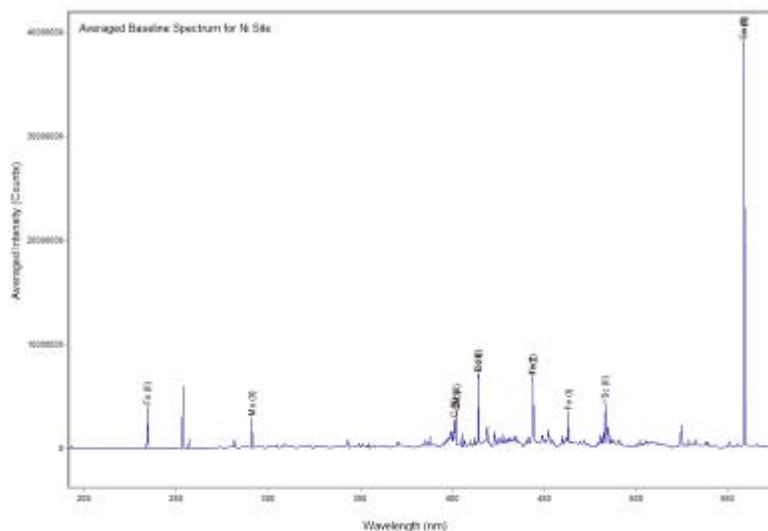
The signal-to-noise ratios were not adequate to enable a positive identification of the three elements for the three spiking runs at the Ni site. The spectra appear to have been collected with an incorrect exposure time. They were all observed at a delay time of 7 μs and variable gate widths ranging from 10 to 50 μs. The gate width appears to have little effect on the spectra; the

delay time has some effect but not significant. It is possible an incorrect (too short) exposure time was used considering the results obtained later from Kirksite furnace. No record of the exposure time was taken, however.

Analysis for the Kirksite furnace exhaust, NADEP

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

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

Fig. 4-1
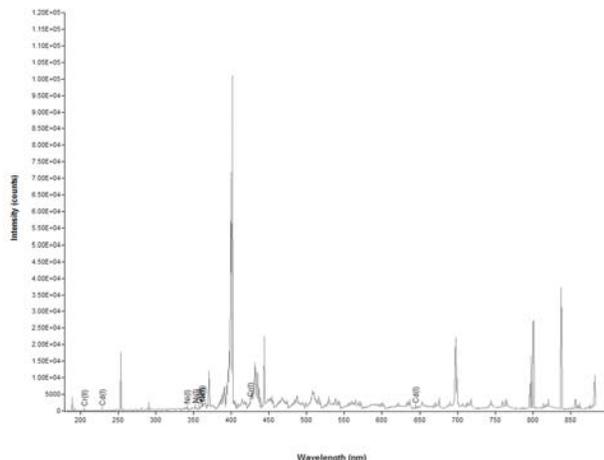
Fig. 4-2
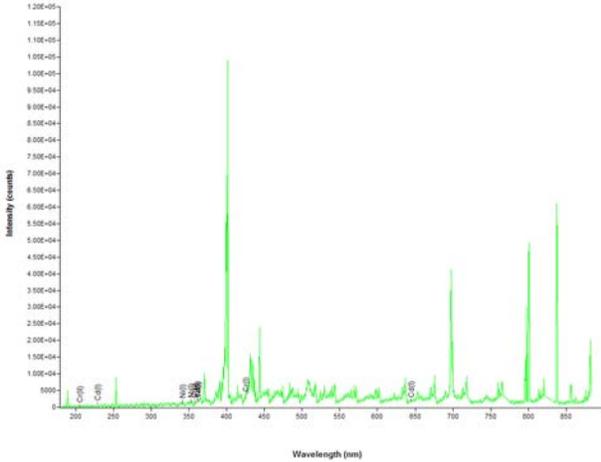
Fig. 4-3
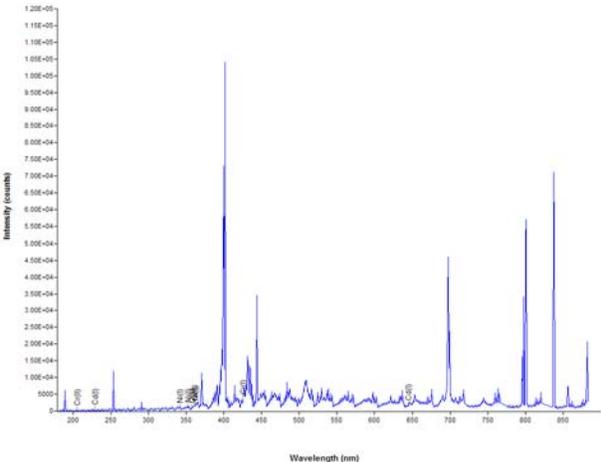
Fig. 4-4
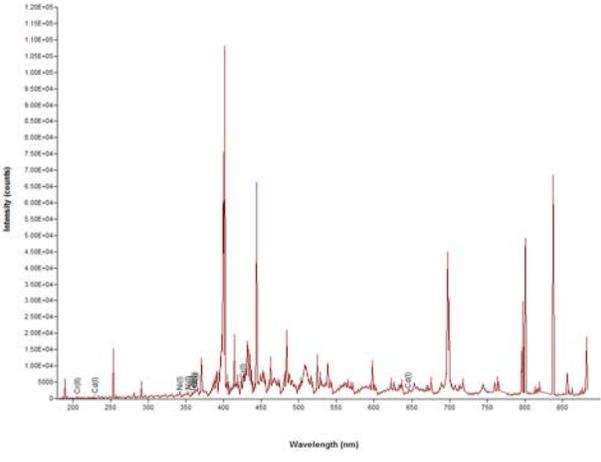
Fig. 4-5
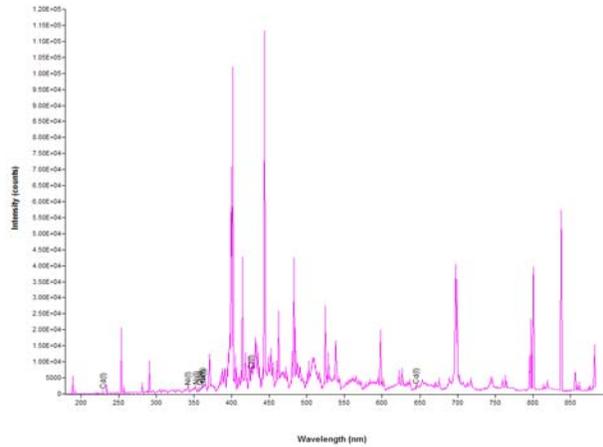
Fig. 4-6
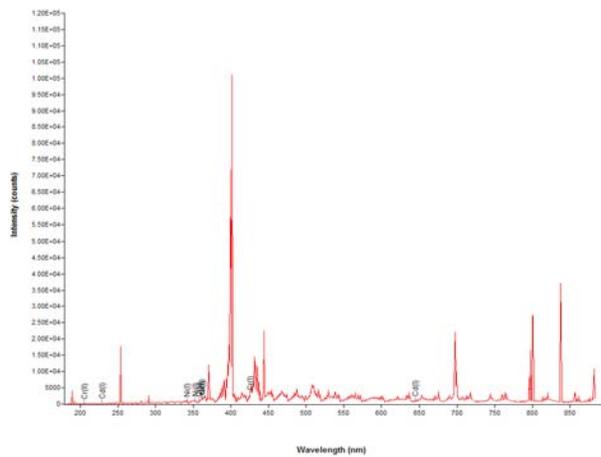
Fig. 5. A 6-point averaged spectrum
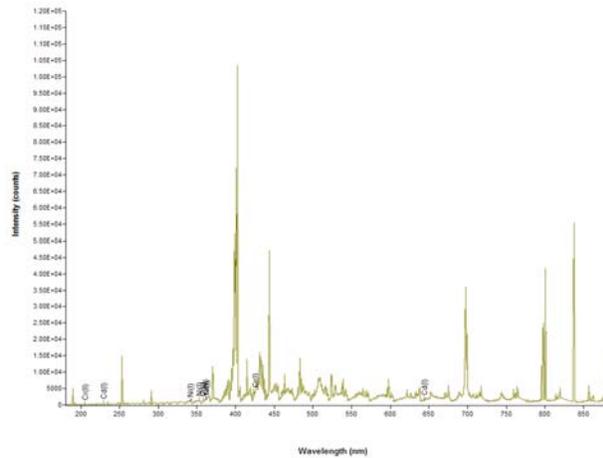
The spectra shown in Fig. 4-1 through 4-6 suggest that at any of the 6 ABF-LIPS probe locations, the observed abundance of target elements, Ni, Cd, and Cr, were reasonably low based on the corresponding peak heights. The differences in the peak heights of the spectra suggest that the flow is not evenly distributed across the duct at the sampling point, or that the concentration of metals varied with time.

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

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

Fig. 6-1. A spectrum between 430nm and 550 at point 1.
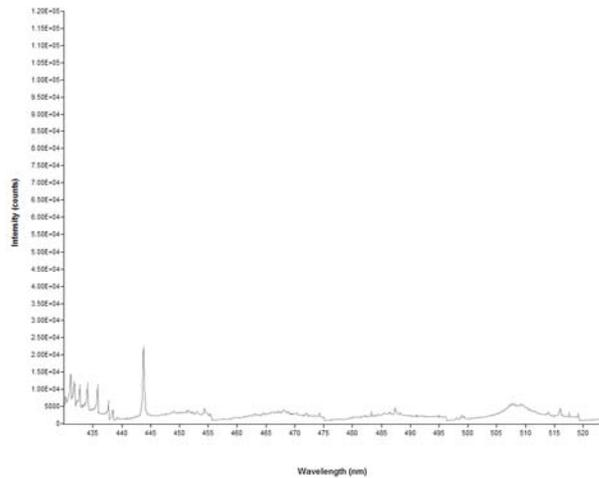
Fig. 6-2. A spectrum between 430nm and 550 at point 2.
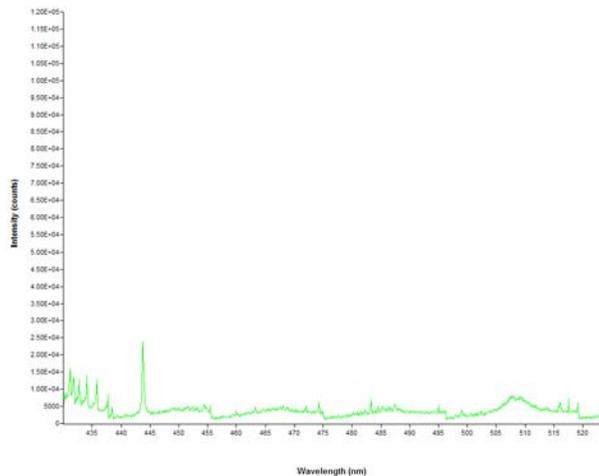
Fig. 6-3. A spectrum between 430nm and 550 at point 3.
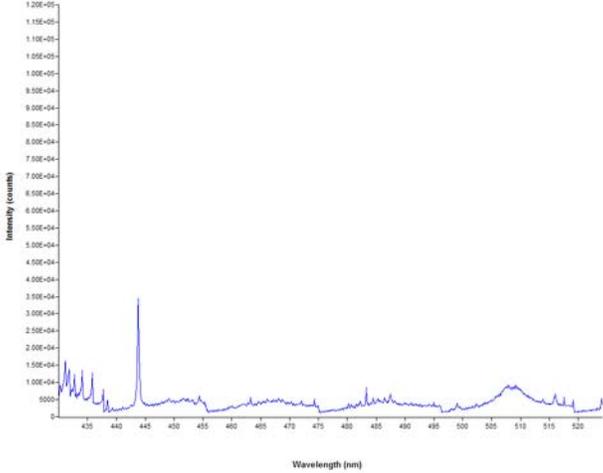
Fig. 6-4. A spectrum between 430nm and 550 at point 4.
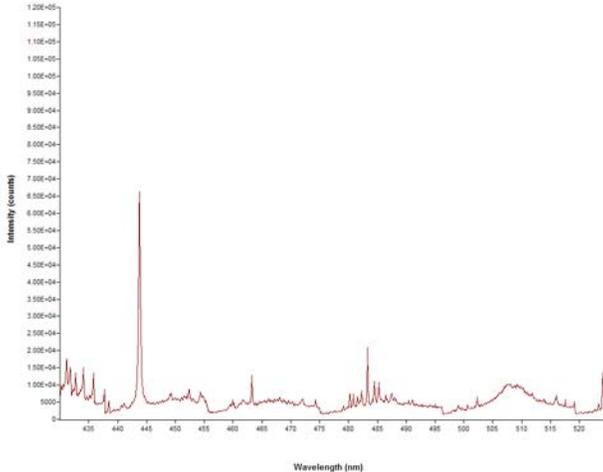
Fig. 6-5. A spectrum between 430nm and 550 at point 5.
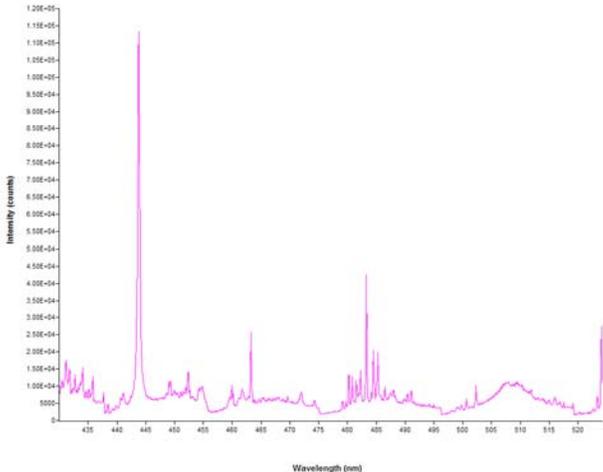
Fig. 6-6. A spectrum between 430nm and 550 at point 6.
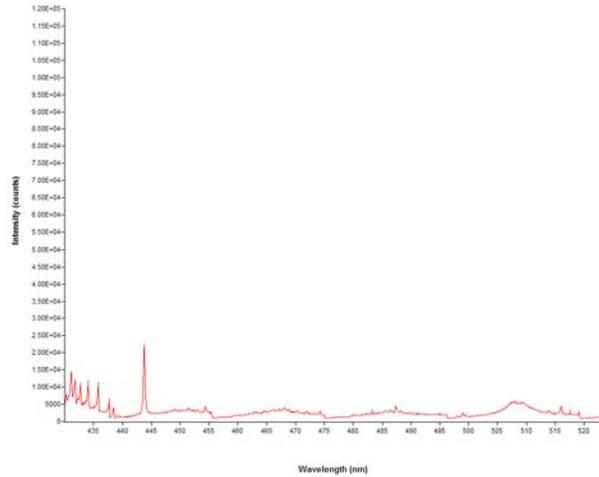
Fig. 7. An averaged spectrum for the window between 430 nm and 550.
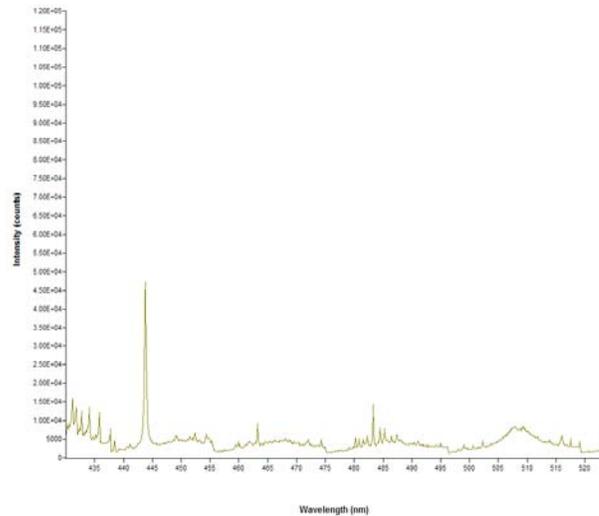
Low Spike Condition – The baseline emissions were spiked with the L (low concentration) solution which contained 330µg/L of Ni, 150µg/L of Cr, and 153µg/L of Cd. A 6-point test configuration was used for these runs, with 12 minutes at each point for a total of 72 minutes per run. There was a minimum of 3 points taken by ABF-LIPS at each probe location. Fig. 8-1 through 8-6 are the broadband results with baseline (Fig. 5) subtracted. Thus, any peaks shown in these figures would have resulted from the spiking solutions. However, it is important to note that due to variability in the baseline measurements a constant subtraction may not be appropriate for all data.

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

Fig. 8-1. A broadband view of the ABF-LIPS spectrum at point 1. Also marked are the three target elements, Ni, Cd, and Cr. Most of the strong lines (i.e., wavelengths) of these 3 metals are found in between 300 to 500 nm as shown.
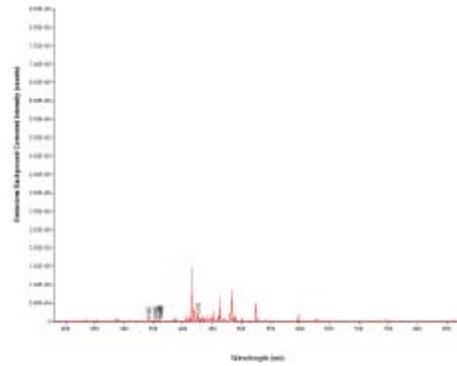
Fig. 8-2. A broadband view of the ABF-LIPS spectrum at point 2.
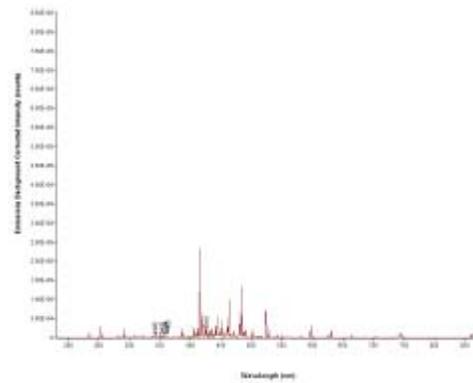
Fig. 8-3. A broadband view of the ABF-LIPS spectrum at point 3.
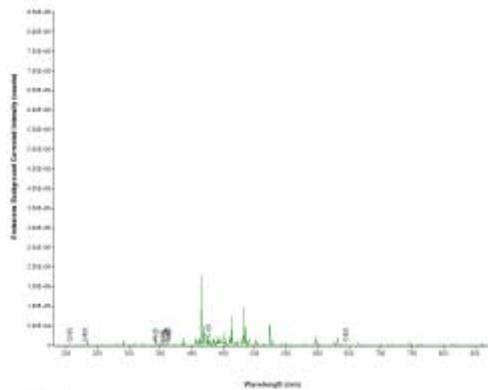
Fig. 8-4. A broadband view of the ABF-LIPS spectrum at point 4.
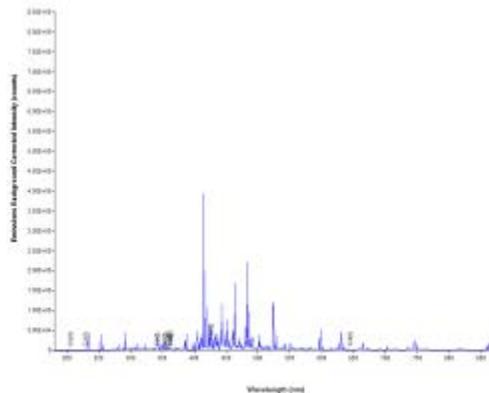
Fig. 8-5. A broadband view of the ABF-LIPS spectrum at point 5.
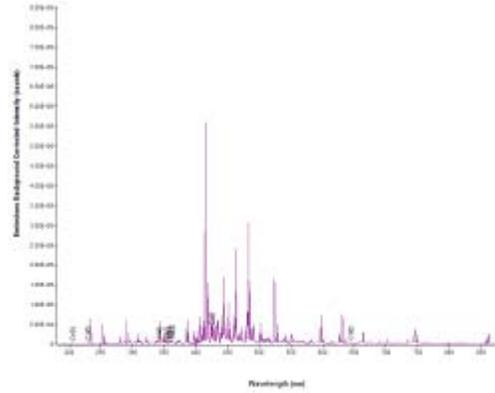
Fig. 8-6. A broadband view of the ABF-LIPS spectrum at point 6
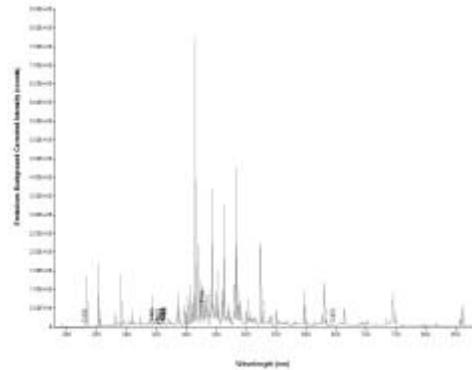
Chromium species were identified within the window of 420-430 nm using the triplet of 425, 427, and 429. The results presented in Fig. 9-1 through 9-6 are baseline-corrected. The peak height of wavelength 425nm was used for quantitative analysis (configuration [3d5(6s)4s-3d]). The flow skewness problem discussed earlier can be seen in Figs. 9-1 through 9-6.

Fig. 9-1. A focused view of the background corrected ABF-LIPS Cr spectrum at point 1. Notice the Cr wavelength triplet at 425, 427, and 429.
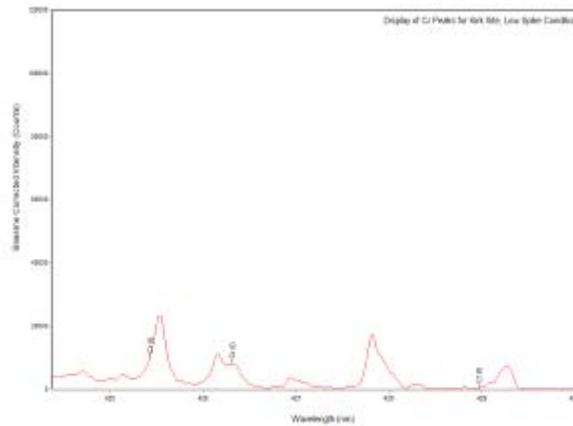
Fig. 9-2. A focused view of the background corrected ABF-LIPS Cr spectrum at point 2. Notice the Cr wavelength triplet at 425, 427, and 429.
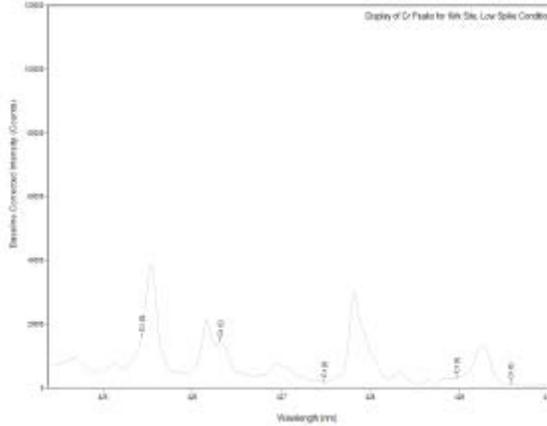
Fig. 9-3. A focused view of the background corrected ABF-LIPS Cr spectrum at point 3. Notice the Cr wavelength triplet at 425, 427, and 429.
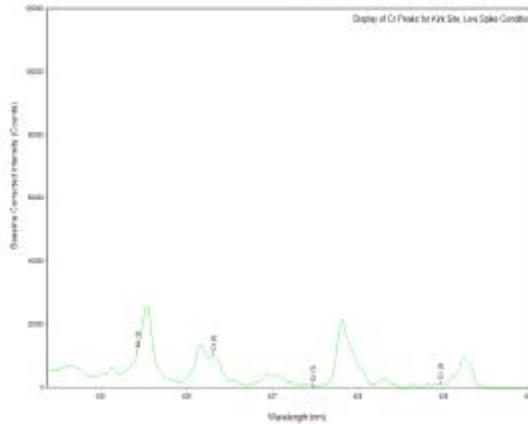
Fig. 9-4. A focused view of the background corrected ABF-LIPS Cr spectrum at point 4. Notice the Cr wavelength triplet at 425, 427, and 429.
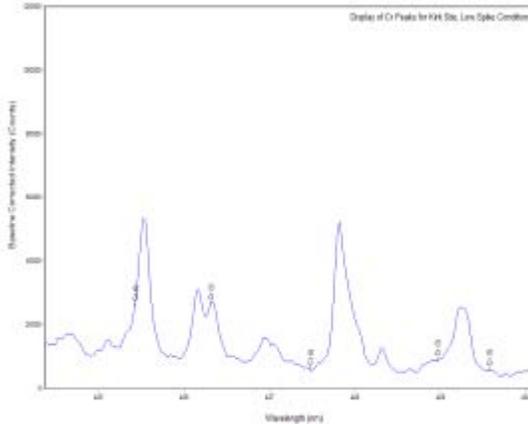
Fig. 9-5. A focused view of the background corrected ABF-LIPS Cr spectrum at point 5. Notice the Cr wavelength triplet at 425, 427, and 429.
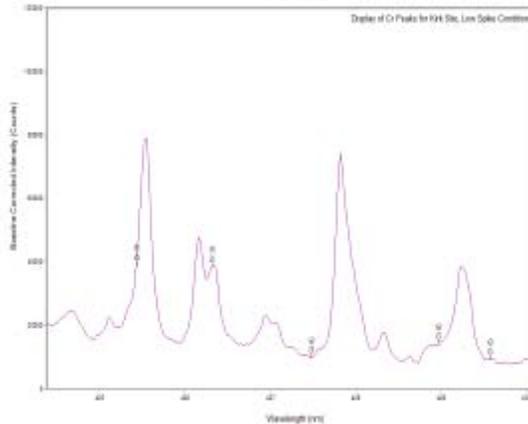
Fig. 9-6. A focused view of the background corrected ABF-LIPS Cr spectrum at point 6. Notice the Cr wavelength triplet at 425, 427, and 429.
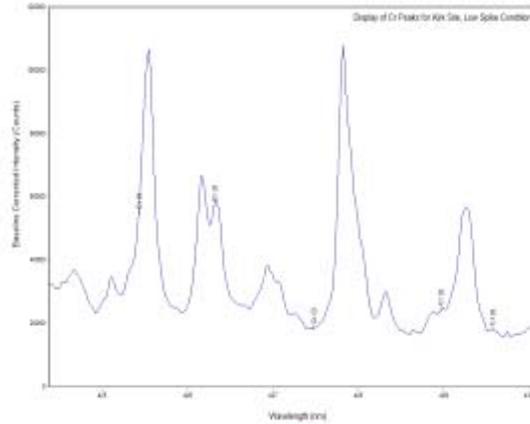
The results for nickel are shown in Fig. 10-1 through 10-6. Again, these results consistently indicate that the flow was skewed toward the duct wall at the locations 5 and 6. The wavelength used to quantify Ni content was 351.06nm [3d9(2D)4s)-3d].

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

Fig. 10-2. A focused view of the background corrected ABF-LIPS Ni spectrum at point 2.
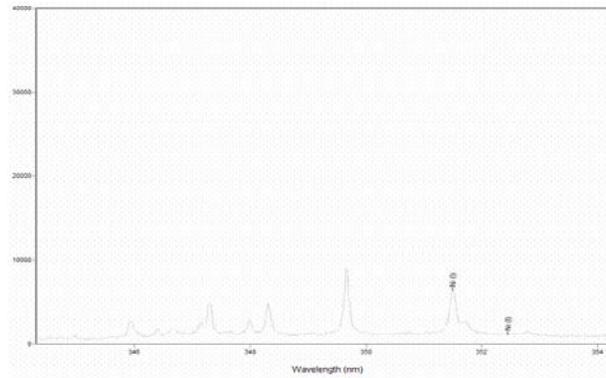
Fig. 10-3. A focused view of the background corrected ABF-LIPS Ni spectrum at point 3.
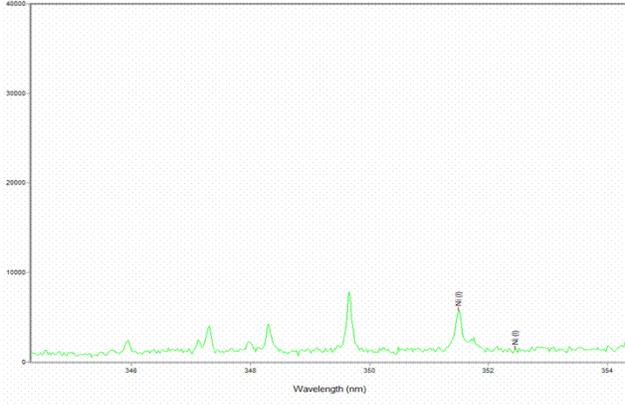
Fig. 10-4. A focused view of the background corrected ABF-LIPS Ni spectrum at point 4.
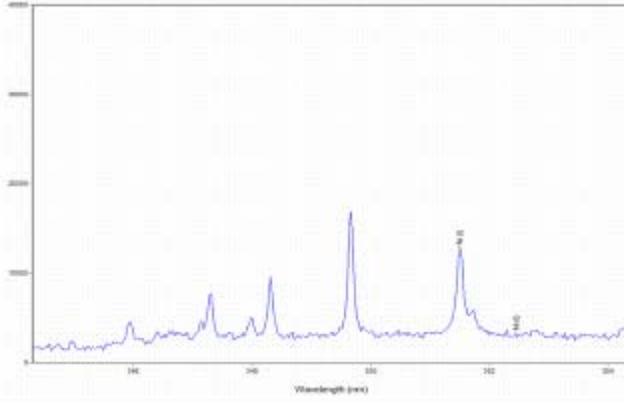

Fig. 10-5. A focused view of the background corrected ABF-LIPS Ni spectrum at point 5.
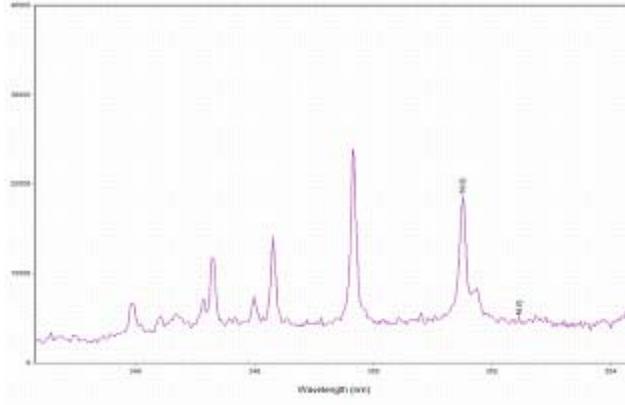
Fig. 10-6. A focused view of the background corrected ABF-LIPS Ni spectrum at point 6.
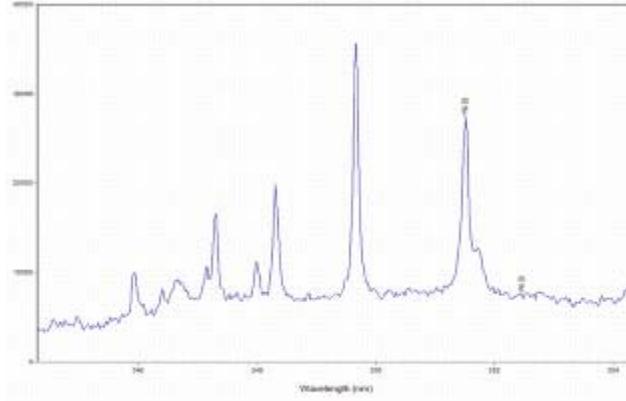
The results for cadmium are shown in Fig. 11-1 through 11-6. These results also indicate that the flow was skewed toward the wall at locations 5 and 6. The wavelengths used to quantify Cd were 537.8 and 734.65 nm.

Fig. 11-1. A focused view of the baseline corrected ABF-LIPS Cd spectrum at point 1.
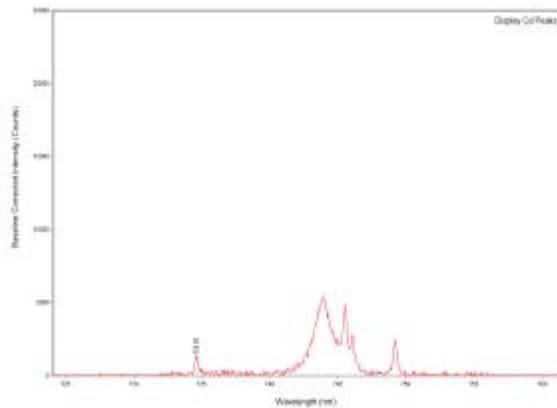
Fig. 11-2. A focused view of the baseline corrected ABF-LIPS Cd spectrum at point 2.
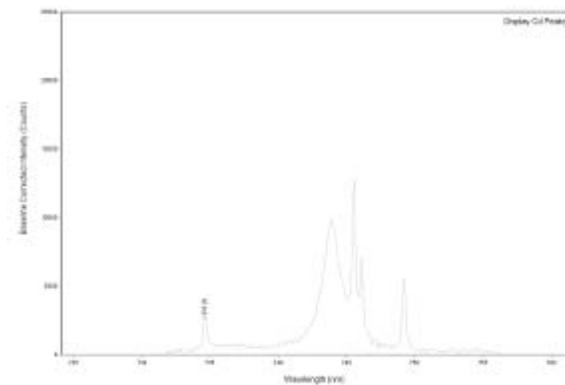
Fig. 11-3. A focused view of the baseline corrected ABF-LIPS Cd spectrum at point 3.
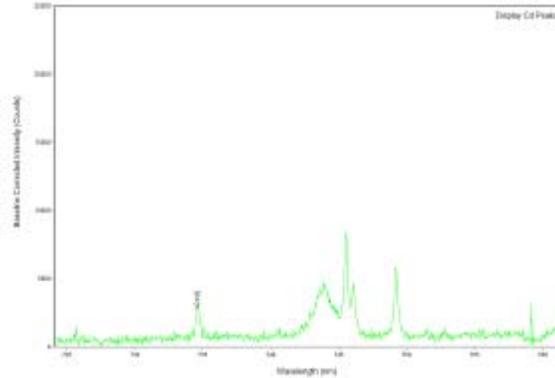
Fig. 11-4. A focused view of the background corrected ABF-LIPS Cd spectrum at point 4.
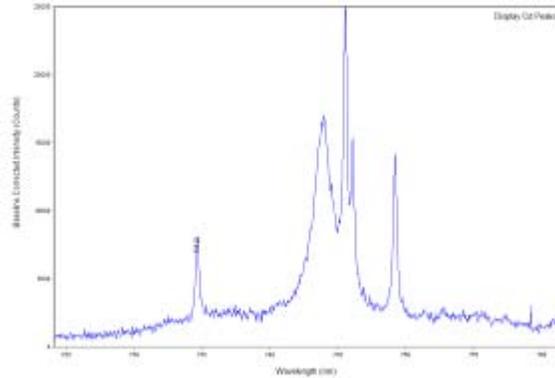
Fig. 11-5. A focused view of the background corrected ABF-LIPS Cd spectrum at point 5.
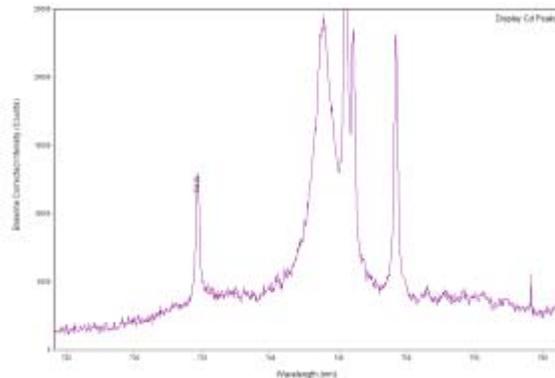
Fig. 11-6. A focused view of the background corrected ABF-LIPS Cd spectrum at point 6.
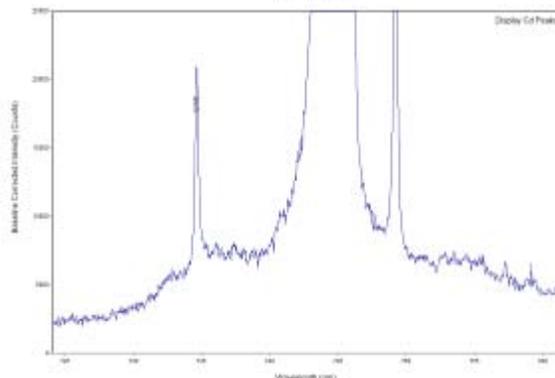
Medium Spike Condition – The Ni concentration in the median spiking solution was prepared to be 702µg/L, Cr 601 µg/L, and Cd 601µg/L. Figs. 12-1 through 12-6 show the broadband view of the ABF-LIPS spectra obtained under the medium spiking condition at the 6

probe locations. It is interesting to note that, based on these 6 plots, the velocity distribution across the duct at the Kirksite furnace appears to be more uniform than previously seen during the baseline and low spiking conditions. There were no significant differences in the peak heights of elements at various probe locations from one side to the other side of the duct wall during the medium spike runs.

Fig. 12-1. Broadband ABF-LIPS spectrum for Kirk site emissions spiked with the median strength solution.
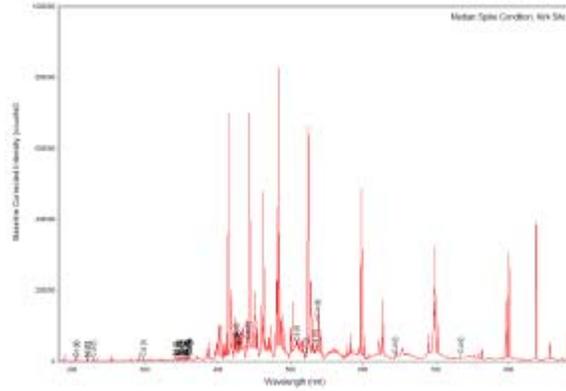

Fig. 12-2. Broadband ABF-LIPS spectrum for Kirk site emissions spiked with the median strength solution.
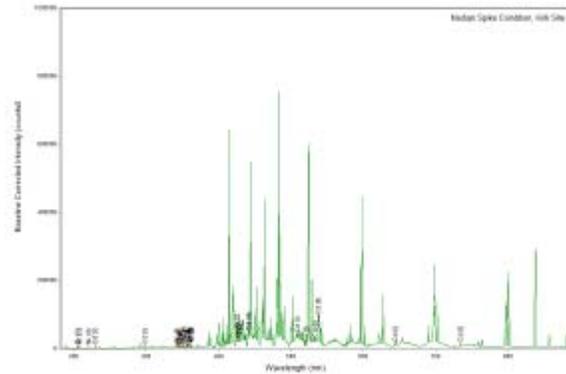

Fig. 12-3. Broadband ABF-LIPS spectrum for Kirk site emissions spiked with the median strength solution.
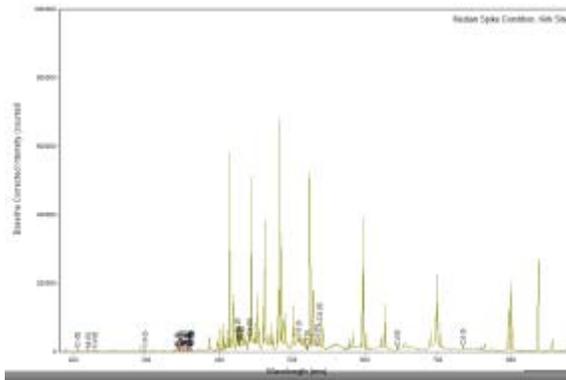
Fig. 12-4. Broadband ABF-LIPS spectrum for Kirk site emissions spiked with the median strength solution.
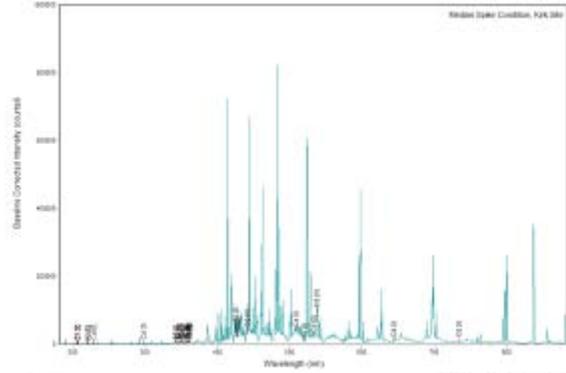
Fig. 12-5. Broadband ABF-LIPS spectrum for Kirk site emissions spiked with the median strength solution.
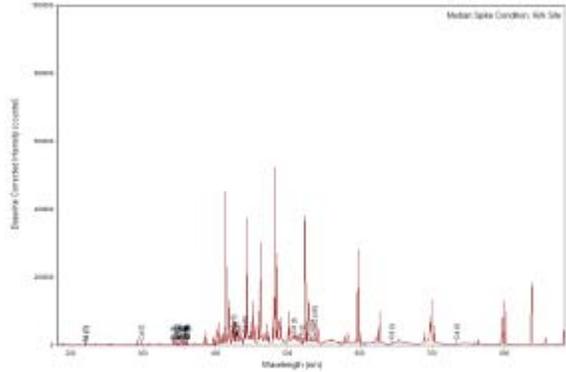
Fig. 12-6. Broadband ABF-LIPS spectrum for Kirk site emissions spiked with the median strength solution.
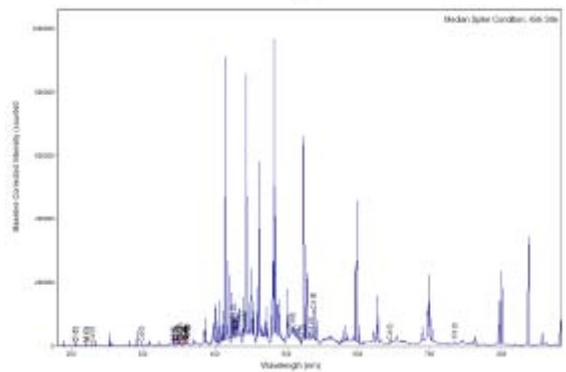
The nickel, chromium, and cadmium concentrations for spiked aerosols are determined from the peak-height readings at their characteristic wavelengths (351.5nm for Ni, 425.5nm for Cr, and 537.8nm for Cd). Table 1 shows the baseline corrected peak-height readings at the three wavelengths for the 6 probe locations taken at the Kirk site under the median spiking condition.

Table 1. Summary Data for The Target Elements at the Kirk Site

Low Spike Solution	330 μg/m^3	150	153
Median Spike	702	601	601
High Spike	2,727	6,000	6,003
Location	Ni, 351.5 nm	Cr, 425.5 nm	Cd, 537.8/734.7[1] nm
L*-1	3,578	23,146	1,305

L-2	6,364	38,185	3,071
L-3	5,782	25,887	3,183
L-4	12,680	51,750	8,030
L-5	18,540	78,795	12,993
L-6	27,400	106,643	20,828
6-point average (μ)	12,391	54,068	8,235
6-point std. dev. (σ)	9,174	32,813	7,503
COV (= σ/μ) in %	74%	60.7%	91.1%
M*-1	11,002	102,672	11,395
M-2	9,828	86,178	8,955
M-3	8,670	78,304	8,293
M-4	11,574	97,236	9,518
M-5	7,649	53,044	5,225
M-6	17,929	103,164	9,378
6-point average (μ)	11,109	86,766	8,794
6-point std. dev. (σ)	3,642	19,187	2,032
COV (= σ/μ) in %	32.8%	22.1%	23.1%
H*-1	548	96	-285
H-2	971	1,323	-36
H-3	3,767	5,446	4,090
H-4	2,239	1,343	5,068
H-5	2,394	931	9,009
H-6	1,291	---	9,592
6-point average (μ)	1,868	1,828	6,940
6-point std. dev. (σ)	1,175	2,085	2,765
COV (= σ/μ) in %	62.9%	114.1%	39.8%

Note:
  (i) X^* indicates the spiking condition. L=low; M=median; H=high.
  (ii) 734.71-nm wavelength was used for low-spiking condition, while 537.8 nm was used for both median and high spiking conditions.

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

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

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

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