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INNOVATIVE
TECHNOLOGY
Summary Report   DOE/EM-0548

Compact High Resolution Spectrometer

Characterization, Monitoring, and Sensor
Technology Crosscutting Program

Prepared for
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Compact High Resolution Spectrometer

OST/TMS ID 1564

Characterization, Monitoring, and Sensor Technology Crosscutting Program

Demonstrated at
Ames Laboratory
Ames, Iowa
Diagnostic Instrumentation and Analysis Laboratory
Mississippi State University
Starkville, Mississippi

Purpose of this document

Innovative Technology Summary Reports are designed to provide potential users with the information they need to quickly determine whether a technology would apply to a particular environmental management problem. They are also designed for readers who may recommend that a technology be considered by prospective users.

Each report describes a technology, system, or process that has been developed and tested with funding from DOE's Office of Science and Technology (OST). A report presents the full range of problems that a technology, system, or process will address and its advantages to the DOE cleanup in terms of system performance, cost, and cleanup effectiveness. Most reports include comparisons to baseline technologies as well as other competing technologies. Information about commercial availability and technology readiness for implementation is also included. Innovative Technology Summary Reports are intended to provide summary information. References for more detailed information are provided in an appendix.

Efforts have been made to provide key data describing the performance, cost, and regulatory acceptance of the technology. If this information was not available at the time of publication, the omission is noted.

All published Innovative Technology Summary Reports are available on the OST Web site at http://ost.em.doe.gov under "Publications."

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SECTION 1

SUMMARY

Technology Summary

This report describes the cost, performance, and other key characteristics of an innovative technology component, the Compact High Resolution Spectrometer (CHRS) (OST Reference Number 1564).
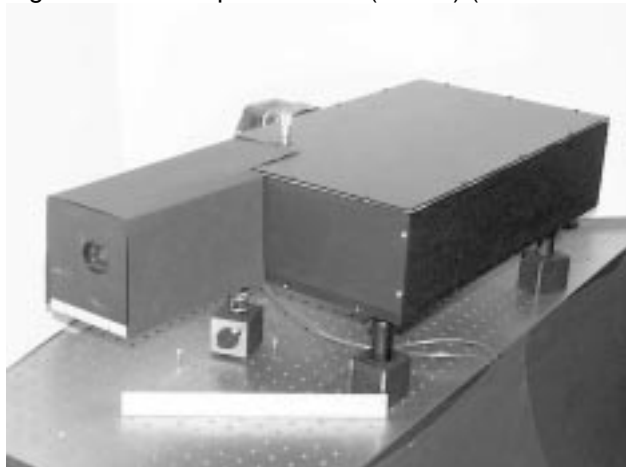

Figure 1. Photograph of the CHRS on an optical bench. It is 36 inches long by 12.5 inches wide by 5.5 inches high and weighs only 46 pounds — less than one-tenth the size and weight of a conventional spectrometer with comparable resolution.

Problem
The principal application of the CHRS is as a component of a Continuous Emissions Monitor (CEM), where it analyzes, detects, and measures the light produced when off-gas emissions from the thermal treatment of mixed waste are stimulated by plasma, spark, or focused laser excitation, or the light that is absorbed when it is passed through such off-gas emissions. The measured characteristics of that light, i. e., the intensities at characteristic wavelengths, allow the CEM to provide continuous measurements of the concentrations of toxic elements present in the off-gas emissions.

CEMs are needed to continuously monitor the performance of mixed waste thermal treatment facilities, providing assurance and documentation that such facilities are continuously operating in compliance with

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regulatory emissions standards. The principal target application area for the CHRS is as a component of a multi-metals CEM capable of monitoring the volatile metal, mercury (Hg), two semi-volatile metals, cadmium (Cd) and lead (Pb), and three low-volatile metals, arsenic (As), beryllium (Be), and chromium (Cr). The U. S. Environmental Protection Agency (EPA) has classified these metals as hazardous air pollutants (HAPs) and has proposed and promulgated new regulations limiting their emission from hazardous waste combustors (HWCs) (EPA 1996, EPA 1999). The new regulations promulgate revised emission standards and clearly establish CEMs as the preferred[1] method for compliance monitoring. The new regulations are commonly referred to as the MACT rule because the emission limits are based on what the agency has determined is the current Maximum Achievable Control Technology (MACT).

The MACT rule includes provisions for the optional use of CEMs for the 6 toxic elements listed above. Furthermore, to provide an incentive for the use of CEMs, the rule does not require waste feed characterization requirements for these elements when CEMs are used. The final MACT rule encourages the use of CEMs to secure the increased assurance of compliance with emissions standards afforded by continuous monitoring systems (EPA 1999).

Currently, there are no commercial CEM technologies that have been demonstrated to be capable of meeting all the performance requirements and data quality objectives proposed by EPA.

The DOE has several incinerator facilities that will be subject to the proposed regulation, when it comes into effect:

- Consolidated Incineration Facility (CIF) at the Savannah River Site (SRS),
- Waste Experimental Reduction Facility (WERF) at the Idaho National Environmental and Engineering Laboratory (INEEL),
- Toxic Substances Control Act Incinerator (TSCAI) at the Oak Ridge Reservation (ORR), and
- Idaho Nuclear Technology Engineering Center (INTEC) at the INEEL.

Local site treatment plans and the *Accelerating Cleanup: Paths to Closure* plan (DOE 1998) require continued operation of these facilities.

DOE incinerators that treat mixed waste also have to monitor any emissions of alpha-emitting materials, including isotopes of actinide elements, e. g., uranium (U) and plutonium (Pu). Currently, DOE uses HEPA filters or other state-of-the-art air pollution control equipment[2] to control actinide emissions and uses high volume air samplers and laboratory analysis of the filters from those samplers to monitor the same. However, in accord with the EPA compliance monitoring hierarchy, it would clearly be advantageous if a single CEM could monitor both the MACT elements and the actinides.

The conventional technology for measuring elemental emissions in stack gases is EPA Method 29 (EPA 1996b). However, Method 29 is not a continuous monitoring technique. It is a protocol for determination of metals emissions by collection of samples from a gas stream and for laboratory analysis of those samples. Method 29 is used during test burns to verify compliance for a specific range of combustion conditions and feed stream conditions. Method 29 typically requires sampling times of one to four hours, involves long analysis turnaround times, is fairly labor intensive, requires skilled laboratory staff for analyses, and provides little assurance to stakeholders that catastrophic releases do not occur, particularly during those more common times when Method 29 sampling is not being conducted. In addition, the costs for trial burns and the necessary analyses of the waste feed stream are high.

Implementation of CEMs that meet EPA performance requirements will minimize the need for trial burns and extensive feed characterization. CEMs will also give continuous, rapidly updated information on treatment operation, providing operator feedback and assuring compliance with emissions limits.

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[1] The top tier of the compliance monitoring hierarchy is the use of a continuous emissions monitor for that HAP or standard. In the absence of a CEM, the second tier is the use of a CEM for a surrogate of that HAP or standard and, when necessary, setting some operating limits to account for the limitations of using surrogates. Lacking a CEMS for either, EPA sets appropriate feed and operating parameter limits to ensure compliance and requires periodic testing of the source (EPA 1996, p. 17417).

[2] At the DOE TSCA incinerator, for example, the air pollution control equipment includes a quench chamber, venturi scrubber, packed bed scrubber, two ionizing wet scrubbers in series, an induced draft fan, and the exhaust stack.

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Demonstration Summary

This demonstration summary covers the period March 1997 through September 1999.

The capabilities of the CHRS were documented in a number of separate demonstrations described in Section 3 of this report. Because the CHRS is a technology component, it was appropriate that most of the demonstrations were in a laboratory environment, culminating in pilot-scale field demonstrations of the CHRS as part of a complete multi-element CEM system.

The laboratory demonstrations documented the basic performance characteristics of the CHRS. They showed the CHRS performance was comparable to that provided by conventional instruments with much greater size, weight, and cost.

The first field demonstration was performed in September 1997 at the EPA rotary kiln incinerator simulator at Research Triangle Park, North Carolina. That demonstration tested a first generation UV spectrometer as part of the air ICPAES CEM demonstrated by researchers from the Diagnostic Instrumentation and Analysis Laboratory (DIAL), Mississippi State University. The spectrometer was based on the high resolution interferometric spectrometer (HiRIS) developed earlier for actinide measurements using ICPAES. Although the actinide monitor had performed extremely well, the UV version exhibited a number of limitations as a detection system for a multi-element CEM. First, it had insufficient resolution for monitoring light emitted from the air-ICP. Secondly, it utilized a photomultiplier tube detector, and that limited the speed at which data could be accumulated for multi-element monitoring. Thirdly, the optical coating used in the interferometer portion of the HiRIS limited its useful range to only a few nanometers in the UV, significantly limiting the resolution and sensitivity for the detection of a number of the target elements. The limitations identified during this test lead to the development of the CHRS in the following fiscal year. The CHRS addresses all these shortcomings and has since replaced the 1 m spectrometer that the DIAL team had used as the standard spectrometer in the air ICPAES system.

The second field demonstration was performed at the DIAL facility in September 1999 (Baldwin et al. 1999). There, the CHRS was demonstrated as part of a CEM that employed a continuous sampling air-ICP system. The demonstration included monitoring toxic metals in stack gas from the combustion of fuel oil and air in the DIAL combustion test stand while exhaust samples were simultaneously collected using EPA Reference Method 29. The CEM results were available continuously during the monitoring. However, because the RM-29 samples required analysis at an off-site analytical laboratory, the results from those samples were not available until several weeks later. For the metals and metal levels observed at DIAL, the CEM results compared favorably with those obtained by the reference method (See Section 3 of this report).

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Other

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TECHNOLOGY DESCRIPTION

Overall Process Definition

Major Features

The CHRS is an echelle grating spectrometer with an acousto-optic tunable filter (AOTF). The grating disperses the emission spectra in high orders (84 through 178) and provides high spectral resolution because resolving power is proportional to the order number. The AOTF provides grating-order selection. An array detector detects the dispersed emission.

Figure 2 shows a photograph of the internals and a schematic drawing of the CHRS. The AOTF portion of the instrument (on the right-hand side) selects light from a narrow wavelength region (0.1 to 0.6 nm wide) and transmits that light to the echelle grating portion of the spectrometer (left-hand side). The enclosure separates the AOTF portion of the CHRS from the echelle grating portion of the system to minimize scattered light.
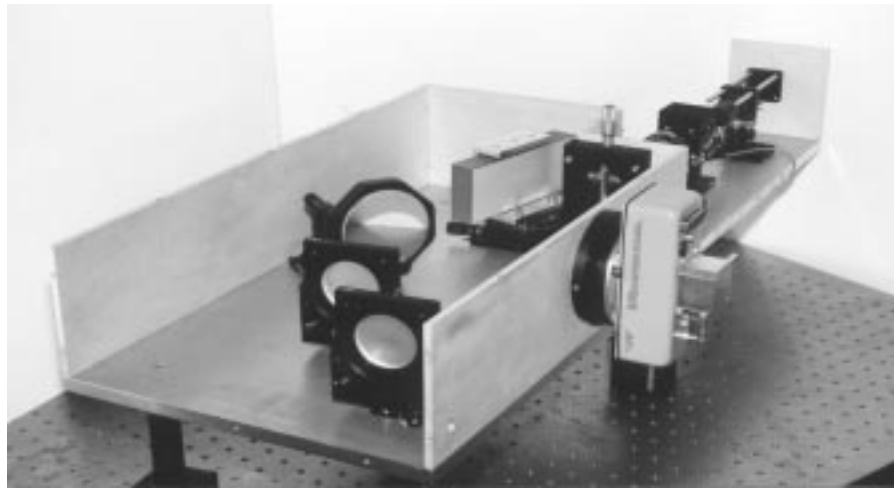
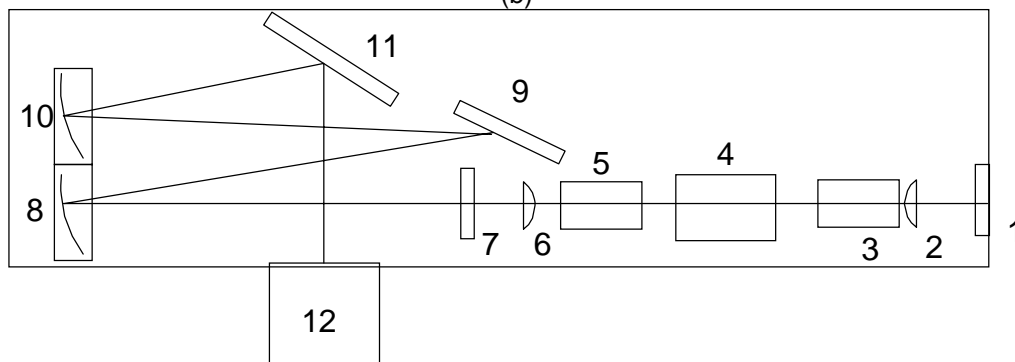Figure 2. (a) Photograph of the CHRS (with enclosure covers removed) on an optical table with holes on one-inch centers and (b) schematic diagram of the same. The numbered components in the schematic are (1) input aperture, (2) collimating lens, (3) polarizer, (4) AOTF, (5) polarizer, (6) imaging lens, (7) slit, (8) collimating mirror, (9) echelle grating, (10) focusing mirror, (11) flat folding mirror, and (12) detector.

AOTF

The AOTF is a quartz crystal device that selects a narrow wavelength region of emitted light and rotates its polarization by 90 degrees (Tran 1992). Placed between two crossed polarizers and tuned by changing an applied radio frequency, the AOTF transmits only a selected wavelength region to the echelle grating. The AOTF is operated using a 12 W rf driver that is tunable from 250 to 90 MHz. This tuning range results in an AOTF wavelength range of 200 to 425 nm. The drive frequency is controlled through a parallel port connection to a personal computer. The wavelength tuning of the AOTF is calibrated using 20 to 50 emission lines from an argon ICP over the entire wavelength range. The observed wavelength and frequency pairs yield a wavelength calibration with an accuracy of approximately 0.05 nm. The AOTF is water-cooled, using a thermostatically controlled loop. The bandwidth of the light transmitted through the second polarizer varies from 0.1 nm at 200 nm to 0.6 nm at 425 nm. This bandwidth is much less than the width of an order of the echelle grating. Therefore, the AOTF serves as an order-selecting device for the echelle grating. It allows extremely rapid (milliseconds) sequential or simultaneous selection of wavelengths with no moving parts.

Echelle Grating Spectrometer

The adjustable entrance slit for the echelle portion of the spectrometer is employed with a width of 15 or 25 micrometers and a height of approximately 3 mm. The light transmitted through the slit is collimated by the first mirror and reflected onto the echelle grating. The grating used in the CHRS operates in orders 84 through 178 order and all these orders are spatially superimposed. However, as previously described, the AOTF portion of the spectrometer transmits only light from a narrow wavelength region (less than the width of one order) and therefore functions as an order-sorter. The reflected beam is focused at the detector using another spherical mirror. To simplify the mounting of the detector on a rectangular enclosure, a flat folding mirror is located between the imaging mirror and the detector (See Figure 21).

Detector

Most of the data in this report were obtained using a Spectrum One CCD-2000 detection system from Instruments SA, Inc., Edison, NJ. The detector is a back-thinned, 2000 by 800 pixel array, cooled to -35 °C with an integral dual-stage thermoelectric cooler. Some initial data were taken using a Model 1453 PDA from EG&G Instruments, Princeton Applied Research, Oak Ridge, TN. The Model 1453 PDA is a linear array of 1024 diodes, each 25 by 2500 micrometers in size. The PDA was cooled to -10 °C with a single-stage thermoelectric cooler. The CCD is significantly more sensitive than the PDA, due to significantly higher quantum efficiency and lower readout background. In both cases, the detector was mounted on an adjustable flange on the side of the spectrometer enclosure, so that the position and rotation of the detector array could be adjusted for optimum resolution.

Software and Control

The spectrometer is controlled and data are accumulated and analyzed using a custom software package that was developed using LabWindows/CVI (National Instruments, Inc., Austin, TX). The software package allows the operator to calibrate and tune the wavelength of the AOTF and to accumulate data using either the CCD or PDA detection system. The software package also includes support for real-time spectral monitoring, accumulation of spectra with background subtraction, monitoring the time evolution of individual peak intensities, calibration and determination of concentrations for multiple analytical lines in a rapid sequential manner, determination of concentrations using the method of standard additions, and unattended continuous monitoring of multiple analytical lines.

System Operation

- CHRS operation, data collection and reporting are performed automatically, under computer software control.
- The CHRS is easy to operate, and can be operated by a technician familiar with the use of personal computers. Training can be completed during a single one-day session.
- A trained technician is needed to perform periodic maintenance tasks such as an annual wavelength calibration.
- Electrical energy is the only expendable used in operation of the CHRS. The maximum total power requirement (for CCD, AOTF, and laptop computer) is 235 Watts, 110 VAC.

- The quartz AOTF requires water-cooling; if there is no "building supply" then a small recirculator is required.
- The CHRS generates no secondary waste.

SECTION 3

PERFORMANCE

Demonstration Plan

The capabilities of the CHRS were documented in a number of separate demonstrations described in Table 1, below. Because the CHRS is a technology component, it was appropriate that most of the demonstrations were performed in a laboratory environment, culminating in pilot-scale field demonstrations of the CHRS as part of a complete multi-element CEM system.

Table 1. CHRS demonstrations

Demonstration	Location	Date
Spectral resolution	Ames Laboratory	June 1998
Imaging quality	Ames Laboratory	August 1998
Method detection limits	Ames Laboratory	August 1998
Mercury CEM capabilities	Ames Laboratory	February 1999
CEM capabilities with DIAL air ICPAES	EPA Research Triangle Park	September 1997
CEM capabilities with DIAL air ICPAES	DIAL	September 1999

Results

Demonstration of imaging quality

The imaging quality of the CHRS was tested in two ways: (1) recording the spectrum produced with various slit widths when the CHRS was illuminated with light from a helium-cadmium laser; (2) comparing the actual spectrum produced by the CHRS with the spectrum calculated using ray-tracing theory. The results of these tests, shown in Figures 2 and 3, show that the CHRS provides high quality imaging, even though it uses only relatively simple, lower cost components.
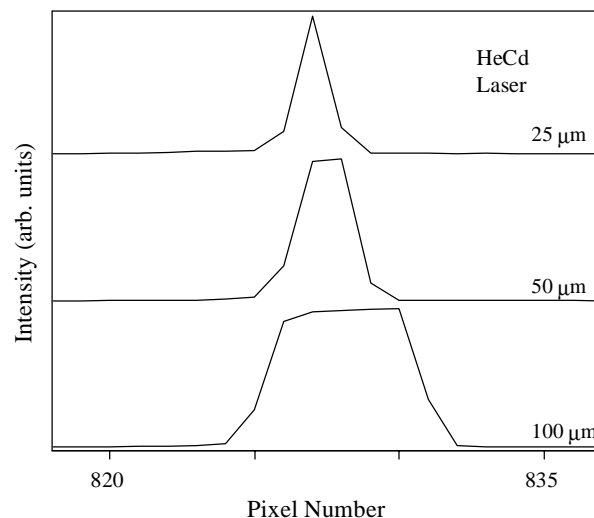

Figure 2. Slit image at the PDA detector (25 micrometer wide pixels) when the CHRS (slit widths indicated in the figure) is illuminated with a helium-cadmium laser (441.56 nm).
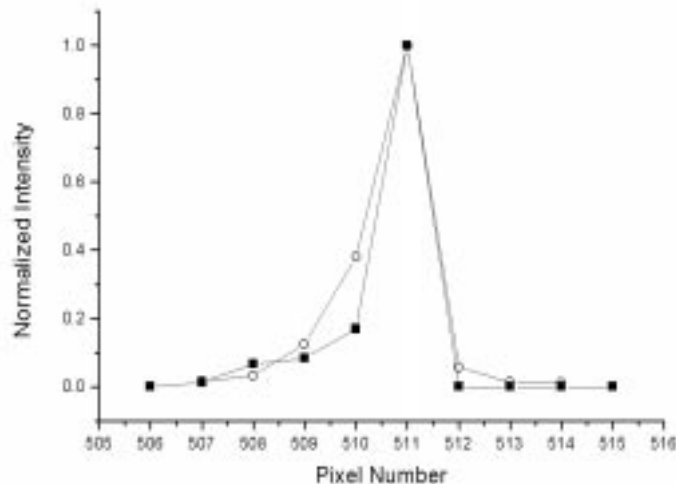
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Figure 3.   Helium-cadmium laser emission at 441.56 nm as observed with the CHRS with PDA detector and 25 micrometer slit width (circles) and as calculated by ray tracing (squares).

Demonstration of high resolving power (spectral resolution)

For CEM applications, a high resolution spectrometer is required for the following reasons:

1.   The gas streams to be monitored consist of relatively complex mixtures with potentially complex spectral interferences. For example, unless resolution is adequate, the large number and density of emission lines arising from even moderate levels of iron degrade the ability to detect and distinguish smaller, but important levels of toxic elements in the sample stream.

2.   The generation of a plasma in an air sample stream excites intense and complex molecular spectra as well as atomic spectra. These will limit the sensitivity (signal to noise ratio) of plasma-based atomic emission techniques unless a high resolution spectrometer is employed.

3.   The most sensitive or useful spectral lines of the elements to be monitored may be so close to each other that a high resolution system is required to distinguish between them. For example, cadmium (Cd) and arsenic (As) have strong emission lines at 228.802 and 228.812 nm, respectively. With a separation of only 0.010 nm between peaks, these lines are only useful for monitoring if they can be resolved. Also, for monitoring radionuclide emissions, it is important to resolve the emission lines of different isotopes in order to measure not just concentration but also the radioactivity of a sample stream. For example, the radioactivity of emissions containing uranium (U) may be determined by resolving the U-235 and U-238 (naturally occurring isotopes) emission lines at 424.412 and 424.437 nm, respectively.

The demonstration results shown in Figures 4 and 5 show that the CHRS has high resolving power. The data in Figure 4 show that the CHRS fully resolves the most sensitive emission lines of cadmium and arsenic. No other system has demonstrated such capability in the comparative tests of CEM capabilities conducted so far. In fact, failure to resolve these two cadmium and arsenic lines has been a relatively common occurrence in those tests.

Using the usual expression for resolving power,

$$R = \lambda/d\lambda,$$

where λ is the wavelength of one of the lines and $d\lambda$ is the wavelength difference between two just-resolved lines, the demonstrated resolving power is at least 22,880. Additional, more comprehensive measurements yielded an observed resolving power of approximately 50,000 (Baldwin et al. 1998). This is as good as that ordinarily achieved by a 1.0 to 1.5 meter (m) spectrometer.

Figure 5 shows data demonstrating the ability of the CHRS to fully resolve the emission lines of uranium-235 and uranium-238. Such resolution is required for continuous monitoring of uranium isotope emissions.
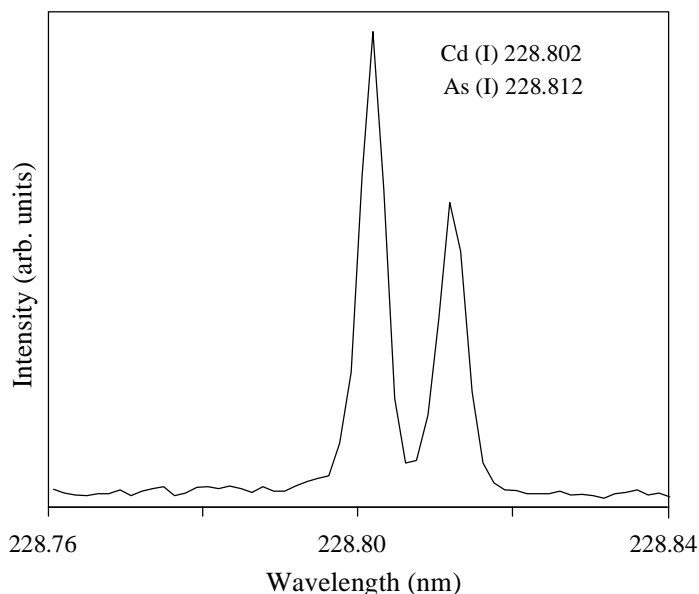
Figure 4.   ICP emission spectra obtained with the CHRS, showing near baseline resolution of the Cd (I) 228.802 and As (I) 228.812 nm emission lines. For this test, a solution containing only As and Cd was introduced to the ICP; the As concentration was 20 times the Cd concentration.
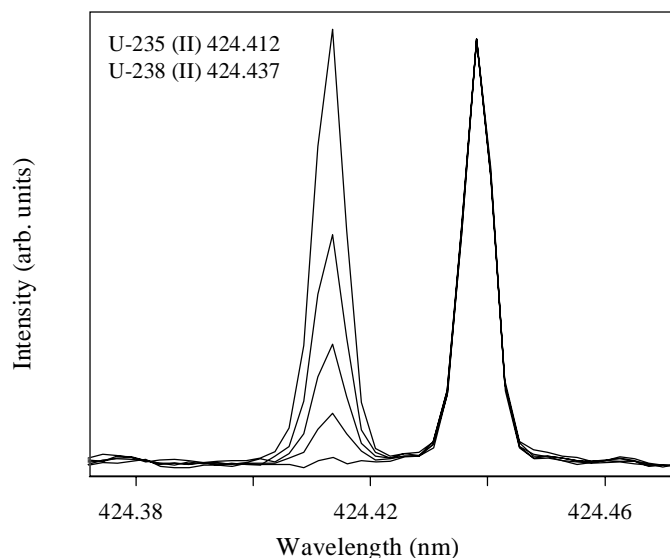
Figure 5.   CHRS ICP emission spectra showing resolution of uranium (II) isotope emission lines for U-235 at 424.412 nm and U-238 at 424.437 nm for mixtures containing 100 ppm U-238 and 0.7, 10, 25, 50, and 100 ppm U-235.

The bandpass of the AOTF is sufficiently narrow that several features from different orders can be imaged simultaneously without interference. For example, the spectra of the most useful lines for As, Be, Cd, Cr, Hg, Pb, and U may all be imaged simultaneously with no interference between the different orders. This capability is illustrated in Figure 6.

Figure 6. ICP emission spectrum showing the ability of the CHRS to simultaneously detect the most useful emission lines for As, Be, Cd, Cr, Hg, Pb, and U, with no interference from overlapping orders.

Demonstration of method detection limits

Limits of detection for ICP emission lines of a number of the elements addressed by the MACT rule are shown in Table 2. The third column in this table lists the solution detection limits (in ppm) for these emission lines as measured using the AOTF-echelle spectrometer. The fourth column is a l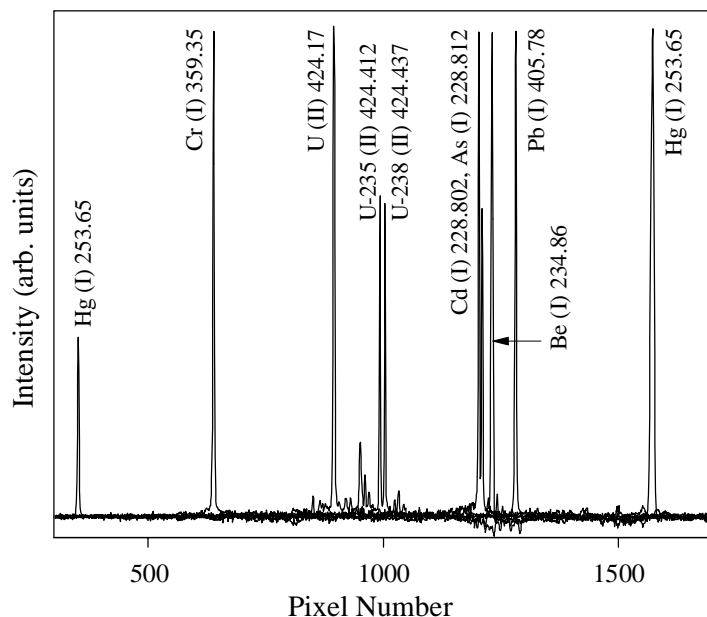ist of detection limits for the same lines as measured using a 1 m focal length Czerny-Turner spectrometer and a PMT detector (Winge, Peterson, and Fassel 1979). The fifth column is the ratio of these detection limits. All of the ratios for wavelengths greater than 275 nm are within an order of magnitude of unity.

Table 2. Measured limits of detection (LOD) for argon-ICP emission lines.

Element (spectrum)	Wavelength (nm)	CHRS Ar-ICP LOD (ppm)	Ar-ICP LOD [a] (ppm)	Ratio [a]
Cd (I)	228.802	0.056	0.0027	20.7
As (I)	228.812	1.7	0.083	20.5
As (I)	234.984	1.7	0.142	12.0
Hg (I)	253.652	1.8	0.061	29.5
Pb (I)	261.418	3.	0.13	23.1
Cr (II)	267.716	0.064	0.0071	9.0
Pb (I)	283.306	0.61	0.142	4.3
Cr (II)	283.563	0.023	0.0071	3.2
Be (II)	313.042	0.00028	0.00027	1.0
Cr (I)	359.348	0.093	0.025	3.7
Pb (I)	405.783	1.1	0.272	4.0

[a] Values from Winge, Peterson, and Fassel 1979; the ratio is the CHRS LOD divided by that from Winge, Peterson, and Fassel 1979.

Below 275 nm, the detection limits reported by Winge et al. are significantly better (smaller) than those determined using the CHRS. The former were limited by the noise associated with the ICP continuum background. Also, because they were determined using a sequentially scanned spectrometer, the noise was estimated as 1% of the background intensity at wavelengths near the selected spectral lines, rather than on actual measured noise levels. This is a reasonable estimate of noise for ICP measurements using a PMT detector and an integration time of several seconds. The detection limits for the CHRS are limited by the shot noise in the dark current from the CCD array detector. This shot noise is constant and independent of the selected wavelength. Improvements in detection limits for the CHRS could be realized by utilizing a lower-noise detector (lower temperature) or by increasing integration times. For convenience, the numbers reported here for the CHRS are based on 1 second integration times. However, integration times of a minute or more are possible (depending on line intensity) and would yield smaller detection limits (i. e., divided by the square root of the integration time in seconds).

In summary, the demonstration results show that the CHRS provides the resolution and sensitivity of a conventional 1.0 to 1.5 meter spectrometer in a package that is less than one-tenth the size and weight of a conventional spectrometer with the same resolution. In fact, based on this performance, the CHRS has replaced the 1 m grating spectrometer previously used as part of the DIAL air-ICPAES CEM system.

Demonstration of CHRS capabilities as a mercury CEM
The principal target application for the CHRS is as a component of a multi-element CEM. However, it also has potential application as part of a mercury CEM.

The first CHRS experiments with mercury measured how much light (at wavelengths characteristic of transitions between the energy levels of mercury atoms) was absorbed when various concentrations of mercury vapor were present between a light source and the CHRS. When the light source is a mercury hollow cathode or electrodeless discharge lamp, this is an atomic absorption spectrometry (AAS) measurement. In fact, since no heat is required or used to vaporize the mercury, it is a CVAAS (cold vapor atomic absorption spectrometry) measurement.

An inexpensive mercury pen lamp was selected as the light source for the measurements. This type of mercury lamp provides much higher emission intensities at the wavelengths of interest than continuum light sources and, with the CHRS, is ideal for the mercury CEM application, using AAS with multiple-wavelength background correction. Figure 7 shows the CHRS detection (in several orders) of numerous mercury emission lines from the mercury pen lamp. Figure 8 illustrates increasing absorption of mercury radiation at 253.65 nm by increasing concentrations of mercury vapor in an optical cell between the mercury pen lamp and the CHRS.

The first CHRS measurements of mercury vapor (in a 10 cm pathlength cell) yielded a detection limit of approximately 20 micrograms/m^3. A practical mercury CEM would likely use a 1 m pathlength cell and provide a detection limit of 2 micrograms/m^3. A CHRS-based mercury CEM system is unique because it can, with a single light path and detection system, measure signal, background, and interferences, simultaneously, thus enabling corrections for both light scattering and absorbing interferants.

Field demonstration of CHRS capabilities as part of a multi-element CEM
The key demonstration of the CHRS is as the detection system for an air-ICPAES CEM used to monitor heavy metals in incinerator off-gases. Two such demonstrations have been performed: (1) at the EPA Incineration Research Facility, Research Triangle Park, NC, in September 1997; (2) at the Diagnostic Instrumentation and Analysis Laboratory (DIAL), Mississippi State University, Starkville, MS, in September 1999.

The baseline technology for the metal emissions monitoring application is EPA Method 29, batch sample collection (with a filter and impinger solutions) followed by laboratory analysis. Typical sample collection times are one hour or more, and the analytical laboratory reports are usually not available until one or two weeks after the samples have been submitted. The CHRS-equipped air-ICPAES system provides measurements of the toxic metals contents of the sampled gases with results reported once per minute or faster. Validation of the CEM method is performed by obtaining continuous measurements of the concentrations of the analytes in a flue gas stream while simultaneously sampling the same stream using the baseline (reference) method. The results from the CEM are averaged over the sampling time used for the reference method and compared with the single value obtained using the reference method.

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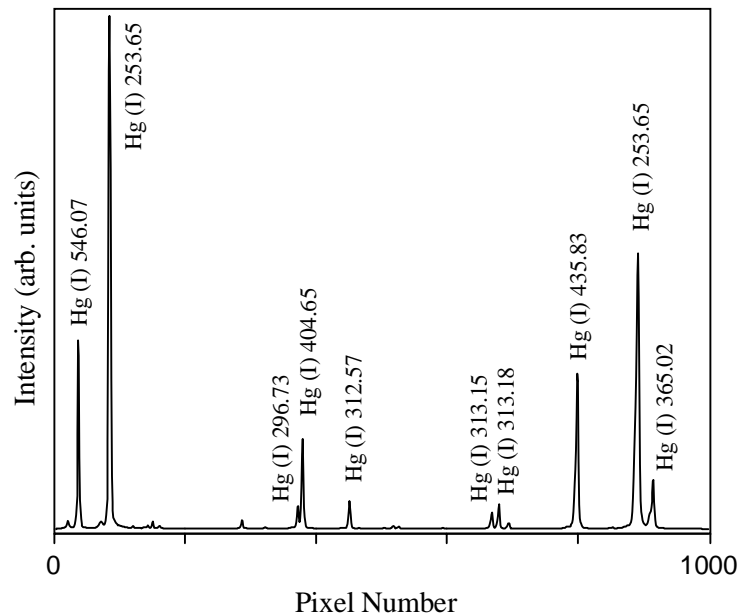
Figure 7.   Illustration of CHRS measurement (in several orders) of numerous mercury emission lines from a mercury pen lamp. No AOTF was used for order selection in the spectrum shown here.
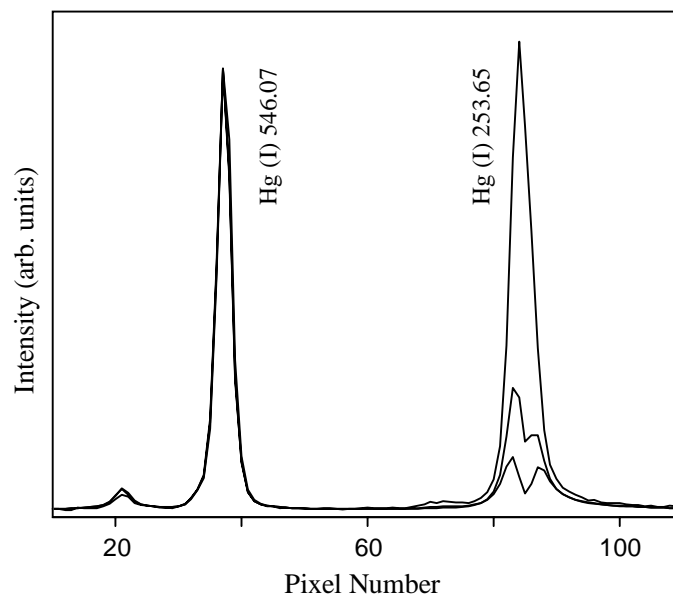
Figure 8.   Intensity of emission from a mercury pen lamp transmitted though an optical cell containing different concentrations of mercury vapor. The intensity of the mercury emission line at 253.65 nm decreases with increasing mercury vapor concentration in the cell because mercury atoms in the vapor absorb light of that wavelength. The intensity of the mercury emission at 546.07 nm does not decrease with increasing mercury vapor concentration because mercury atoms in the vapor do not absorb light of that wavelength. Also, because the background levels in the vicinity of the absorption are measured simultaneously, changes in the background level caused, for example, by SO2 interference can be corrected easily and automatically.

The first field demonstration (test) of the CHRS as the detection system for an air-ICPAES CEM occurred at an early stage in the development of the CHRS. The results showed (DOE-ID 1998) that additional work was needed before such a CEM would meet the proposed EPA Draft performance specification for a multi-metals CEM (EPA 1996, pp. 17499-17502).

In the second demonstration, at DIAL during the week of September 12, 1999, the CHRS was demonstrated as part of a complete multi-metals CEM system that also included a newly developed reduced-pressure sampling system and an air-ICP. The capabilities of the system were tested by monitoring metal emissions in the exhaust from a fuel oil-air combustor. This was the first field test for the new CEM; the demonstration test plan was ambitious, involving several significant tasks for the one-week period: (1) integration of a compact solid-state ICP power supply and its impedance-matching network with the reduced-pressure sampling system and air-ICP; (2) integration of the early model CHRS delivered to DIAL in FY 1998 with the reduced-pressure air-ICP system; and (3) connection of the reduced-pressure continuous sampling air-ICP system to a sampling port on the DIAL combustion system and operation of the complete CEM for metals monitoring while simultaneously collecting samples using EPA Reference Method 29. All these tasks were completed during the demonstration; the collected samples were sent to a certified laboratory for quantitative analysis by EPA reference methods. A report providing a complete technical description of the demonstration, results and planned future activities has been distributed (Baldwin et al. 1999).

Table 3 compares the analysis results obtained using the CHRS-based air-ICP CEM system with those obtained using the EPA Reference Method — sampling and laboratory analysis. In summary, the results of this second demonstration were far better than those of the 1998 demonstration. The CHRS results for all the metals measured were within 20% or less of the values obtained by the EPA Reference Method.

Table 3. Analysis results from the CHRS-based Air-ICP CEM system and the EPA Reference Method

	CHRS-based Air-ICP CEM Result (μg/dscm)	EPA Reference Method Result (μg/dscm)
Beryllium	73	70
Cadmium	n.d.	75
Chromium	63	60
Lead	56	70
Mercury	n.d.	66

During the September 1999 testing at DIAL, the CHRS-equipped air-ICPAES CEM did not detect cadmium and mercury at levels that were measurable using the baseline (EPA reference method)[3]. The summary reason is that the limits of detection during this one-week field test were not as good as those observed in previous tests. It is not appropriate to offer a lengthy explanation here. Instead, please see Appendix C, where limits of detection and experimental details are reported for the September 1999 test and several earlier tests. Here, it may be sufficient to note, as also outlined in Appendix C, the principal investigator projects dramatically improved limits of detection for the CHRS-based multi-element CEM in the very near future, and that those LODs (with the exception of As) compare favorably with the recently promulgated emission standards for hazardous waste combustors (EPA 1999). The emission standards and projected LODs are shown in Table 4, below.

Because arsenic is not a common contaminant in DOE mixed waste, the high LOD for arsenic is not likely to diminish the applicability of the CHRS in a multi-element CEM at DOE mixed waste incineration facilities. There, some level of feed stream characterization may provide adequate assurance of compliance with respect to control (absence) of arsenic emissions.

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[3] Arsenic was not even included in the test because of its high limit of detection.

Table 4. Emission standards for hazardous waste combustors (HWCs) (EPA 1999) and projected limits of detection.

		Standard for existing HWCs (µg/dscm)	Standard for new HWCs (µg/dscm)	Projected LOD(s) [b] (µg/dscm)
Mercury	Hg	130	45	2
Low Volatility Metals	As + Be + Cr	97 [a]	97	300(As), 0.004(Be), 0.3(Cr)
Semi-Volatile Metals	Cd + Pb	240	24	15(Cd), 2(Pb)

[a] The table states, for example, that the emission standard for the total of the As + Be + Cr concentrations is 97 µg/dscm.

[b] Please see Appendix C, Table C-2.

SECTION 4

TECHNOLOGY APPLICABILITY AND ALTERNATIVES

The target problem for the CHRS is the continuous monitoring of toxic elements in off-gas emissions from mixed waste incinerators. Other envisioned DOE applications include hot-cell analyses of isotopic abundances for materials containing or contaminated with U or Pu, on-line monitoring in process ducts, and other field applications requiring high resolution optical measurements.

Competing Technologies

- **Baseline –**
  The baseline technologies for optical spectrometry with sufficient resolution for use as a CEM are
  – Tunable grating spectrometers with 1.0 to 1.5 m focal length;
  – Polychromators with 0.75 to 1 m focal length.

  EPA Method 29 is the baseline method for measurement of toxic elemental emissions from hazardous waste combustors. This involves collection of samples from the off-gas stream, packaging and documentation of the samples according to EPA sample handling and chain-of-custody requirements, and shipping them to an off-site laboratory for analysis. The analyses are performed using one or more of the methods described in Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, SW-846 Update III (EPA 1995). The laboratory analysis methods employed as part of Method 29 may include ICAP, ICAP-MS, AAS, CVAAS, and or GFAAS. The baseline method does not provide real-time results because the sampling time is typically one to four hours per sample and the elapsed time between the collection of samples and the availability of the analysis results is typically measured in weeks.

- **Other competing technologies –**
  For optical spectrometry, other competing technologies include the following.
  – Echelle spectrometers with orthogonal dispersion for order-sorting (Barnard et al. 1993, Scheeline et al. 1991, Pilon et al. 1990).
    These systems employ cross-dispersion, using a low-order, low-dispersion grating, or a prism, to spatially separate the spectral orders in a direction orthogonal to the echelle dispersion. They can detect emission from a number of individual orders of the echelle simultaneously or sequentially, using multiple, movable, or two-dimensional array detectors. Most provide wavelength coverage from approximately 180 to 800 nm, but complex optical configurations are required and some reduction in resolution is tolerated to achieve broad wavelength coverage.
  – Fabry-Perot interferometer (FPI) with tunable monochromator for order-selection.
  – FPI with AOTF for order-selection.

  When applied with an air-ICPAES for continuous emissions monitoring, the CHRS competes with the following other technologies:
  – The commercially available Thermo Jarrell Ash TraceAir, an air+argon ICP AES system with a 0.75 m vacuum or argon-purged polychromator;
  – Microwave-induced plasma AES with various spectrometer-detector systems;
  – Laser-induced breakdown AES with various spectrometer-detector systems; and
  – Spark-induced breakdown AES with various detector systems.

- **CHRS advantages and disadvantages as compared to the baseline for optical spectrometry –**
  – The CHRS is approximately one-tenth the size and weight of baseline instruments that provide comparable resolution.
  – The cost of the CHRS is in the lowest quartile of the cost range for baseline instruments with comparable resolution and is approximately one-half the cost of the most costly baseline instrument. Details are provided in Section 5 of this report.

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- Because the CHRS is considerably smaller and lighter than the baseline instruments providing comparable resolution, its space and cost-of-space requirements are less than those of the baseline instruments.
- The CHRS switches wavelengths very rapidly as compared to the tunable grating spectrometer. That's because the CHRS uses electronic tuning, whereas the tunable grating spectrometers use mechanical tuning (moving parts). The rapid tuning ability makes the CHRS ideal for continuous monitoring of multiple emission features at widely spaced wavelengths.
- The CHRS is more flexible than polychromators, which require moving the detector components to change the selection of lines.
- The CHRS is easier to align than a polychromator because it has fewer adjustable parts.
- The sensitivity of the CHRS is limited by the transmission efficiency of the AOTF. The crossed polarizers only transmit one polarization, and the AOTF transmission efficiency varies from 20 to 50% over its wavelength range. Hence, overall transmission efficiency is only 10 to 25%. Despite this limitation, the detection limits are good, probably because the increased resolution provided by the CHRS tends to improve the signal to noise ratio.
- The f/8 design aperture of the AOTF limits the light throughput of the CHRS. Faster collection optics have more leakage through the crossed polarizers. However, the background (and leakage) are typically recorded with the spectrum of interest, and are then subtracted to determine signal levels. Thus, despite the moderate f-number and leakage, the detection limits achieved with the CHRS compare favorably to those of larger conventional spectrometers.
- The CHRS limits of detection are slightly poorer overall than those of the baseline instruments.
- The current model of the CHRS only monitors one small wavelength region at a time (like a grating spectrometer) but a polychromator can monitor several. Future CHRS models will be able to monitor several wavelength regions simultaneously.

- **CHRS advantages and disadvantages as compared to other competing technologies for optical spectrometry –**
  - Compared to conventional echelle grating spectrometers that utilize cross-dispersion gratings or prisms, and which provide comparable resolution, the CHRS provides advantages in reduced size, weight, and cost, reduced size and complexity of optical components, and reduced off-axis aberrations and light losses. In addition, optical alignment of the system is easy and little or no subsequent adjustment is required.
  - The CHRS has less complex spectrum detection and interpretation requirements than the echelle with orthogonal dispersion. Consequently, it can also function with a lower cost detector.
  - The CHRS exposes the detector to less stray light than the echelle spectrometer with orthogonal dispersion. This minimizes light-induced deterioration of optical components, which is important for ICPAES applications.
  - The current CHRS is a very rapid sequential spectrometer rather than a simultaneous instrument like some echelle spectrometers with orthogonal dispersion. However, a multi-band AOTF device with multi-bandpass capability has already been demonstrated in the laboratory. These multi-band devices will support simultaneous detection of multiple emission lines in future CHRS systems.
  - The performance of Fabry-Perot interferometers (FPIs) depends on the performance of mirrors; the reflective properties of the mirrors depend on wavelength. FPIs work well and provide excellent resolution for wavelengths greater than 400 nm, however, at lower wavelengths, where most of the emission lines for the elements of interest here occur, the useful bandwidth becomes so narrow that a specific FPI performs well for only one or two emission lines (elements).
  - The CHRS can tune much more rapidly than an FPI with a tunable monochromator for order-selection.
  - The CHRS supports simultaneous measurement of several emission lines (toxic elements), whereas an FPI generally measures only one at a time.
  - Wavelength calibration for the CHRS, because it is based on observation of several emission lines simultaneously, is much easier than it is for a FPI, where the analyte line of interest is essentially the only available wavelength standard. Because of this, the CHRS is well suited for monitoring concentrations near the limit of detection, whereas systems that use an FPI are poorly suited for such work.

- **CHRS advantages and disadvantages as compared to the baseline when applied with an air-ICPAES for continuous emissions monitoring –**

- The CHRS CEM can provide continuous real-time measurements of the emissions of toxic elements; the baseline technology cannot.
- With collection and laboratory analysis of three samples per day, the baseline method could only roughly approximate the continuous monitoring provided by a CEM. However, as shown in Section 5 of this report, the cost would be approximately 2.5 times the cost of monitoring using a CHRS CEM.
- When a CEM is used, EPA imposes less demanding feed characterization requirements than when the baseline technology is used. Feed stream characterization is not required for hazardous air pollutants that are monitored with a CEM. This can reduce characterization costs and increase waste throughput (and corresponding revenue for commercial treatment facilities).
- When a CEM is used, it must cut off the waste feed automatically when emission limits are exceeded. This is a health and environmental advantage as compared to the baseline.

- **CHRS advantages and disadvantages as compared to other competing technologies when applied with an air-ICPAES for continuous emissions monitoring –**
    - The bandpass of the AOTF is sufficiently narrow (0.2 to 0.6 nm depending on the wavelength) that the CHRS can rapidly measure several features from different orders on a linear array without interference. For example, as illustrated in Figure 6, above, the spectra of the most useful lines of the toxic elements of interest, As, Be, Cd, Cr, Hg, Pb, and U, may all be transmitted to the detector without interference of the different spectral regions selected by the AOTF.
    - The CHRS is approximately one-half the cost and one-tenth the size of the polychromator-based argon/air-ICPAES system.
    - The CHRS with reduced pressure sampling system is capable of continuous sampling and continuous monitoring of offgas from hazardous waste combustors. The TJA polychromator-based argon/air-ICPAES system alternates sampling and analysis periods so it only monitors half time.
    - The polychromator-based argon/air-ICPAES system achieves a better (lower) limit of detection for arsenic than the CHRS does. The former uses an argon-purged spectrometer and hence can monitor the arsenic line 189.0 nm. That line has more intense emission than the arsenic 228.80 nm line monitored by the CHRS.
    - The CHRS monitors all emission lines full time whereas the present microwave plasma systems only monitor a few lines at a time.
    - The CHRS with reduced pressure sampling monitors the entire sampled stream whereas the laser-induced breakdown and spark-induced breakdown systems monitor only a tiny (volumetric) fraction of the sample stream.

Technology Applicability

The CHRS may be used in any application that requires sensitive and high resolution detection of spectral features. As compared to the baseline technology, the CHRS advantages in size, weight, cost, and simplicity make it attractive for field applications and process monitoring applications that require high resolution.

Many of the methods being investigated now for CEMs would benefit from inclusion of the CHRS. Those include, for example, ICPAES, microwave-induced plasma, laser-induced breakdown spectroscopy (LIBS), and spark spectroscopy. The CHRS has already replaced the conventional spectrometer previously used in the air-ICPAES CEM developed at DIAL. It is also a promising candidate for replacing multiple spectrometers currently used in the microwave-induced plasma CEM system developed by Dr. Paul Woskov at MIT. The CHRS will provide superior resolution and wavelength agility in a significantly smaller package than the present system.

Similarly, the CHRS may be used with LIBS, spark, and other plasma sources to improve the resolution, speed, and portability of those methods. For example, the principal investigator has used the CHRS for LIBS analyses of aerosols and solids and has compared the results to ICP analyses using aerosol and laser-ablation sample introduction. Figure 9 shows two spectra: (1) LIBS of paint chip samples and (2) ICPAES of aerosol created by laser ablation of the same samples. Comparison of the two CHRS spectra shows that, in the LIBS case, self-absorption is a problem for the lead line at 405.78 nm. Similar

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observations in other wavelength regions also revealed significant self-absorption for many other strong analytical emission lines; time gating of the observations did not significantly improve the situation. A key fact is that observations using spectrometers with lower resolution would not likely detect the self absorption; in that case, the LIBS technique would have significant calibration problems.

Although significant self-absorption was not observed when LIBS was used for aerosol measurements, previous demonstrations (DOE-ID 1998) have shown that high resolution will likely be needed to avoid spectral interferences that will otherwise limit the accuracy and sensitivity of the LIBS technique.

The CHRS may also be used as a tool for analyzing the isotopic composition of radioactive waste and nuclear fuel materials containing uranium, thorium, or plutonium. One system demonstration currently under consideration would use the CHRS and air-ICPAES system to monitor the levels of uranium in process ducts at a commercial refining operation producing uranium oxide fuel stock from natural ores. The system demonstrated would be the same as that used for multi-metal CEM application at mixed waste incinerators. During the demonstration, the company would be evaluating the system for process control. However, it is also well aware of its applicability for their emission monitoring needs. The site personnel will be looking primarily for how this technique can improve their operation rather than worrying about the rigor and burdens imposed by regulatory compliance expectations. This is the type of demonstration that is likely to lead to increasing application and acceptance of continuous monitoring techniques.
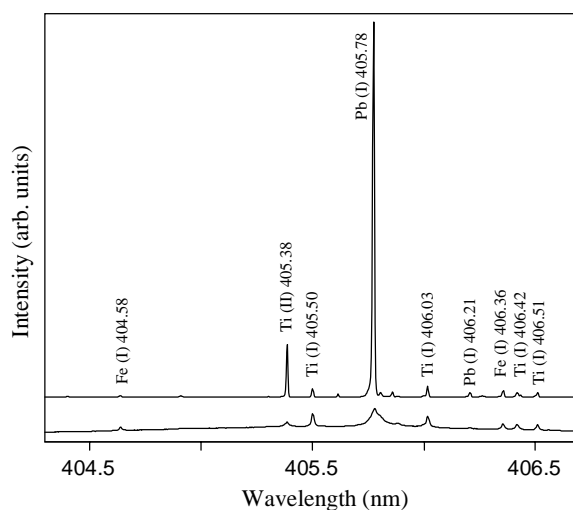
Figure 9. CHRS spectra of paint chip samples containing lead. The lower trace is a laser-induced breakdown spectrum (LIBS). The upper trace is an inductively coupled plasma atomic emission spectrum (ICPAES) of aerosol created by laser ablation of same paint sample.

Another potential application is in passive remote sensing, where high resolution and sensitivity are needed in a device that is compact and sufficiently rugged to be carried in or attached to a plane or helicopter. Because of its relatively small size and weight, the CHRS can also be used to make any laboratory-based high resolution optical technique into a field technique. Such techniques and systems are needed for determining the presence or absence, and measuring the concentration, of hazardous elements in various matrices including groundwater, soil, and gaseous remediation process and effluent streams at hazardous waste sites.

Additional applications are anticipated in areas where conventional laboratory techniques are limited by the resolution of the spectrometers used in commercial instrumentation. These areas include Raman spectroscopy, conventional ICPAES, and atomic absorption.

Patents/Commercialization/Sponsor

Iowa State University has offered the CHRS for licensing and Mississippi State University has offered the air-ICPAES CEM. Although several prominent analytical instrument manufacturers have expressed interest in both technologies, so far, no commercial entity has committed to produce and market either.

The principal investigator has communicated with potential users concerning the production of CHRS systems for individual applications within DOE, such as hot-cell analysis of wastes. Ames Laboratory intends to pursue such production under approved Work-for-Others arrangements.

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Introduction

The main challenge in performing cost-savings analysis for application of the CHRS versus the baseline is the determination of costs for application of the two in one or more realistic application scenarios. This is especially difficult for the principal envisioned application of the CHRS, namely, as a key component in a mercury- or multi-element CEM. In that application, the CEM (if it fulfills performance requirements) provides emissions data which are entirely different from (and much better than) that provided by the baseline approach.

As described elsewhere (French, Priebe, and Haas 1999), the baseline (EPA) approach for limiting the emissions of hazardous air pollutants from hazardous waste combustors (HWCs) uses feed rate limitations and control of facility operating conditions. Facility operators are required to measure and limit the rate of mercury (and other hazardous element) feed and to operate the facility within a range of conditions known to adequately limit the concentrations of the hazardous elements in the stack gas. In this baseline approach, the range of the waste feed rate and the other facility operating conditions under which the facility can perform with acceptably low emissions is established during an EPA trial burn or comprehensive test. The performance of the facility and its associated air pollution control equipment is measured during those tests, which typically last one or two weeks. The regulations require periodic trial burns (every three to five years, depending on the size and type of facility) to verify that the facility continues to meet emissions standards.

The baseline approach (feed and facility characterization and control) uses standard EPA SW-846 laboratory analysis methods for measuring HAPs in the feed. During the trial burn or comprehensive performance tests, EPA method 29 is typically employed for sampling the stack gas and measuring the HAP emissions.

The baseline approach is useful, but it only provides emissions data during relatively short, widely spaced test periods. The emissions are presumed to be under control during the three to five years between tests, but data to confirm this are not available. Clearly this regulatory approach does not provide continuous assurance of compliance with emissions standards. On the other hand, CEMs provide continuous real-time emissions data and, therefore, continuous assurance of compliance. That's why EPA prefers and encourages the use of CEMs.

Methodology

Application Scenarios
The cost analysis considers two application scenarios:

Scenario 1. The CHRS is employed in place of baseline technology for optical spectrometry.
For this scenario, the cost analysis simply compares the cost of the CHRS to the cost of several commercially available baseline spectrometers with comparable resolution.

Scenario 2. The CHRS is employed as a component of a multi-element CEM monitoring As, Be, Cd, Cr, Hg, and Pb during operation of a hazardous waste combustor treating DOE mixed waste in compliance with the EPA MACT Rule.
For this scenario, the cost analysis compares costs for three cases:
1. No CEM is used; standard baseline sampling and off-site analytical laboratory analysis methods are employed.
2. A CHRS-based CEM is employed for continuous monitoring.
3. No CEM is employed, however, standard baseline sampling and off-site analytical laboratory analysis methods are employed in a multiple samples per day manner that

attempts to provide near continuous monitoring that roughly approximates that provided by a CEM.

General Cost Analysis Assumptions

To facilitate understanding and comparison with costs at other sites, all overhead and general and administrative (G&A) costs are omitted from this analysis, both for the innovative technology and for the baseline.

CHRS Costs

The CHRS costs shown in Table 5 were obtained from the Principal Investigator. These are actual costs incurred in procurement of components and assembly of the CHRS. These costs will change (and will likely decrease) as the costs of components, assembly, customization, and integration come under increasing control and as the market size becomes better understood.

Table 5. CHRS costs

Description	Approximate cost ($K)
Complete CHRS system (including desk top computer, monitor, and software for operating the CHRS)	39 (47 for model supporting simultaneous selection of multiple wavelength regions)
On-site installation	5
Documentation & software distribution	6
On-site integration & customization	6

Cost Analysis

Scenario 1. The CHRS is employed in place of baseline technology for optical spectrometry.
Here, the cost analysis compares the cost of the CHRS to the cost of baseline instruments providing resolution and spectrometric wavelength range comparable to that provided by the CHRS. The data are summarized in Table 6.

Table 6. Costs of CHRS and baseline spectrometers that provide comparable resolution.

Spectrometer	Cost, (K$)	Note
CHRS with CCD detector and instrument control and data acquisition software	45	a, b, x
1.0 m spectrometer with 2400 groove/mm, 110 X 110 mm grating, stepping motor controller, CCD detector, and software for spectrometer control, data acquisition and analysis (manufacturer A)	34 to 49	c, y
1.5 m spectrometer with 3600 groove/mm, 120 X 140 mm grating, stepping motor controller and driving software (manufacturer B)	67 to 72	d, y
2.0 m spectrometer with 1800 groove/mm, 250 nm blaze grating, stepping motor controller and CCD detector (manufacturer C)	81 to 83	e, y
1.0 m spectrometer with 2400 groove/mm, 110 X 110 mm grating and two photomultiplier detectors and software for spectrometer wavelength scanning and control, data acquisition and analysis (manufacturer D)	72	f, y
0.75 m, argon-purged polychromator with photomultiplier detectors for simultaneous measurement of six MACT elements (manufacturer E)	94	g, z

(Notes for Table 6 are continued on the following page.)
Table 6 continued
 a Includes $8K CCD detector, instrument documentation and software distribution; does not include on-site installation or on-site integration and customization.
 b $53K for model supporting simultaneous selection of multiple wavelength regions
 c Cost of offered CCD detectors and software ranges from $15K to $32K
 d Includes $5K to $10K for photodiode array detector and data acquisition software
 e Cost of offered CCD detectors and software ranges from $15K to $17K
 f $86K for model including integral ICPAES source

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g   Includes ICPAES source
x   This system has no moving parts. All wavelength selection and data acquisition are performed
     under computer-directed rapid electronic control.
y   In contrast to the CHRS and the polychromator listed last in this table, these systems rotate the
     grating to select different wavelength regions; monitoring cannot be performed while the grating is in
     motion.
z   This system has at least six fixed slits, one for each of the elements to be measured. The
     measurements for the multiple elements (slits) are performed simultaneously. Such systems have
     little ability to measure any other elements that may be of interest unless they are shut down and
     mechanically reconfigured for that purpose.

Cost Conclusions for Scenario 1 ▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀▀

For Scenario 1, use of the CHRS for optical spectrometry, the cost analysis conclusions are as follows.
- As seen in Table 6, the cost of the CHRS (at $45K including an $8K CCD detector, instrument
  documentation and software distribution), is in the lowest quartile of the cost range for baseline
  instruments with comparable resolution and is approximately one-half the cost of the most costly
  baseline instrument.
- The CHRS is considerably smaller and lighter than the baseline instruments providing comparable
  resolution, hence its space and cost-of-space requirements are less than those of the baseline
  instruments.

Scenario 2. The CHRS is employed as a component of a multi-element CEM monitoring As, Be, Cd, Cr,
Hg, and Pb during operation of a hazardous waste combustor treating DOE mixed waste in
compliance with the EPA MACT Rule.
Here, as noted previously, the cost analysis compares the costs for three cases:
1. No CEM is used; standard baseline sampling and off-site analytical laboratory analysis
    methods are employed for trial burns and waste feed characterization (waste and
    process characterization control). The cost details and estimated ten-year life-cycle
    costs for this case are given in Table 7.
2. A CHRS-based CEM is employed for continuous monitoring in addition to baseline
    methods for trial burns and waste feed characterization (waste and process
    characterization control). The cost details and estimated ten-year life-cycle costs for
    this case are given in Table 8.
3. No CEM is employed, however, in addition to using baseline methods for trial burns and
    waste feed characterization, standard baseline sampling and off-site laboratory analysis
    methods are employed for three off gas samples per day, in an attempt to provide near-
    continuous monitoring roughly approximating that provided by a CEM. The cost details
    and estimated ten-year life-cycle costs for this case are given in Table 9. The cost
    estimate for this case is included to provide an estimate of the value (cost) of near-
    continuous monitoring (by baseline methods) roughly approximating that provided by a
    CEM.

Assumptions and Cost Data for Scenario 2 Cases
- Information concerning the actual or assumed details that drive the costs for the three cases
  considered in Scenario 2 are provided in the first two columns of Tables 7 through 9. Most of this
  information needs no additional explanation.
- In accord with information provided by James Dunn of the TSCA Incinerator, Oak Ridge, TN [(865)
  241-3737; e7d@bechteljacobs.org], the Scenario 2 cost analysis assumes four waste samples and
  four stack gas samples are taken and analyzed for a preliminary (or test) trial burn prior to the official
  (for record) trial burn; an additional four waste samples and four stack gas samples are taken and
  analyzed for the official (for record) trial burn. Current federal regulations require a trial burn every 5
  years (at minimum).
- The costs for stack gas sampling and laboratory analysis of the stack gas samples were provided by
  Jeff Ryan, U.S. EPA [Ryan.Jeff@epa.gov]. These were based on the costs incurred during CEM
  testing conducted at EPA RTP in September 1997 and on current price quotations provided by
  Oxford Laboratories, Wilmington, NC. The cost for laboratory analysis of the stack gas samples

includes the cost of routine quality assurance testing. The cost for stack gas sampling ports is not included in this cost analysis because it is considered a plant cost. In any case, it would be the same for the three CEM and baseline approaches considered in the Scenario 2 cost analysis.

- The costs for sampling of the mixed waste feed stream and laboratory analysis of feed stream samples were taken from *Mixed Waste Characterization Document* (INEEL/EXT-97-01009), September 1997; it was assumed that analysis of one feed stream sample per week would be sufficient to adequately characterize the toxic metals content of the feed stream, as required by current regulations.
- The cost analysis assumes the services of a CEM technician are required at the level of two hours per week – to cover weekly routine CEM maintenance and calibration activities. As the CEM technologies mature, this would likely decrease to one hour per week or less.
- The cost analysis assumes the optical detector for the CEM would need replacement every five years (on average).
- The cost analysis assumes CEM consumables, principally calibration materials, would cost approximately $50/week.
- The stated CEM capital cost ($64K) includes a complete CHRS-based CEM for As, Be, Cd, Cr, Pb, and Hg. The cost indicated is for a complete CHRS system supporting simultaneous selection of multiple wavelength regions, desk top computer and monitor, CCD detector, software for instrument control and data acquisition, CHRS documentation, on-site installation, and on-site integration and customization (per Table 5, above).

Cost Conclusions for Scenario 2

- The CHRS-based CEM (Case 2) provides continuous monitoring of multi-metals emissions at less cost than the baseline method (Case 1), which measures emissions only once every five years. The estimated ten-year life-cycle cost is $5.864 for the CHRS-based CEM versus $5.889 million for the baseline method.
- The CHRS-based CEM (Case 2) provides better monitoring (continuous versus near continuous) than application of baseline sample collection and laboratory analysis methods that only roughly approximates continuous monitoring (Case 3) and does so at lower cost (estimated ten-year life-cycle cost of $5.864 million versus $15.551 million).
- The difference between the estimated ten-year life-cycle costs for Case 1 ($5.889 million) and Case 3 ($15.551 million) provides one estimate of the value of the near-continuous emissions monitoring that can be provided when baseline methods are applied in a way that only roughly approximates that provided by the multi-metals CEM. The estimated ten-year value of such near-continuous monitoring, if provided by baseline methods, is $9.687 million.
- The cost of taking feed stream samples – for characterization of the hazardous constituents content – is the principal operating cost for all three Scenario 2 cases. This cost is high because the waste is assumed to contain TRU radionuclides. Hence, all sampling operations must be performed in ways that protect the sampling personnel from those radionuclides as well as the hazardous chemical constituents. This requires the use of engineered barriers such as glove boxes and painstaking attention to safety, hence the high cost.
- EPA does not require feed stream characterization for those hazardous constituents for which a CEM is employed. According to EPA, this is an incentive to encourage the use of CEMs. This is not a large cost incentive for the Scenario 2 CEM application because the estimated ten-year life-cycle (present value) cost for Scenario 2 Case 2 is only reduced by 2.8 percent (from $6.030 million to $5.864 million) when feed stream analysis for hazardous metals is eliminated. The incentive is large enough, however to make the estimated ten-year life-cycle cost for use of the CHRS-based multi-metals CEM $25K (0.4 percent) less than that of the baseline. Reduction or elimination of feed stream sampling costs as well would have a much larger impact, reducing the estimated ten-year life-cycle cost to $0.449 million. However, the regulatory requirement to characterize the feed stream for hazardous materials other than those monitored by a multi-element CEM still has to be satisfied; this means that samples still have to be taken.

Other Conclusions

The key fact concerning use of the CHRS as a CEM component (as in scenario 2) is that it is enabling technology. The characteristics and capabilities of the CHRS enable the creation of CEMs with the performance capabilities needed for compliance monitoring of hazardous emissions. CEMs with those

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capabilities, by providing far more timely and complete information concerning emissions, enable better control of the waste treatment process and the emissions therefrom and, consequently, better protection of human health and the environment. This is the driver for the use of CEMs, not cost or cost avoidance.

- Because the application of CEMs is not driven by cost but by regulations and other non-cost considerations such as protection of human health and the environment, and securing or protecting a "right to operate" granted by the facility neighbors, the comparisons of cost for the Scenario 2 cases can only be said to be interesting, not compelling.

- As additional demonstrations are completed using the CHRS, additional cost data will be generated and more comprehensive cost analyses will become possible.

Table 7. Estimated ten-year life-cycle costs for Scenario 2 Case 1, baseline method.

		Year									
		1	2	3	4	5	6	7	8	9	10
CEM Capital Cost		$0									
Operating Cost											
Trial Burn Cost											
Feed Stream Sampling @$12,000/sample	8 samples	$96,000				$96,000					$96,000
Laboratory Analysis of Feed Stream Samples (for metals) @$366/sample	8 samples	$2,928				$2,928					$2,928
Stack Gas Sampling @ $2000/day	8 days	$16,000				$16,000					$16,000
Laboratory analysis of stack gas samples @$350/sample	8 samples	$2,800				$2,800					$2,800
Total Trial Burn Cost		$117,728				$117,728					$117,728
Ordinary Operating Cost											
Feed Stream Sampling @$12,000/sample	1 sample/week	$624,000	$624,000	$624,000	$624,000	$624,000	$624,000	$624,000	$624,000	$624,000	$624,000
Laboratory Analysis of Feed Stream Samples (for metals) @$366/sample	1 sample/week	$19,032	$19,032	$19,032	$19,032	$19,032	$19,032	$19,032	$19,032	$19,032	$19,032
CEM Technical maintenance service @ $50/hr	~ 0 hr/week	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
CEM Optical Detector replacement @ $10,000/ea	0/5y						$0				
CEM consumables (calibration materials, etc.)	~ $0/week	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Total Ordinary Operating Cost		$643,032	$643,032	$643,032	$643,032	$643,032	$643,032	$643,032	$643,032	$643,032	$643,032
Total Operating Cost		$760,760	$643,032	$643,032	$643,032	$760,760	$643,032	$643,032	$643,032	$643,032	$760,760
Total Annual Cost		$760,760	$643,032	$643,032	$643,032	$760,760	$643,032	$643,032	$643,032	$643,032	$760,760
Total Life Cycle Cost	$6,783,504										
Present Value of Total Annual Cost (Discount Rate = 3.30%)		$760,760	$622,490	$602,604	$583,353	$668,108	$546,677	$529,213	$512,307	$495,941	$567,995
Present Value of Total Life Cycle Cost (Discount Rate = 3.30%)	$5,889,448										

Table 8. Estimated ten-year life-cycle costs for Scenario 2 Case 2, CHRS used as component of a multi-element CEM.

		Year									
		1	2	3	4	5	6	7	8	9	10
CEM Capital Cost		$64,000									
Operating Cost											
Trial Burn Cost											
Feed Stream Sampling @$12,000/sample	8 samples	$96,000				$96,000					$96,000
Laboratory Analysis of Feed Stream Samples (for metals) @$366/sample	8 samples	$2,928				$2,928					$2,928
Stack Gas Sampling @ $2000/day	8 days	$16,000				$16,000					$16,000
Laboratory analysis of stack gas samples @$350/sample	8 samples	$2,800				$2,800					$2,800
Total Trial Burn Cost		$117,728				$117,728					$117,728
Ordinary Operating Cost											
Feed Stream Sampling @$12,000/sample	1 sample/week	$624,000	$624,000	$624,000	$624,000	$624,000	$624,000	$624,000	$624,000	$624,000	$624,000
Laboratory Analysis of Feed Stream Samples (for metals) @$366/sample	None because multi-metal CEM is used	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
CEM technical maintenance service @ $50/hr	~ 2 hr/week	$5,200	$5,200	$5,200	$5,200	$5,200	$5,200	$5,200	$5,200	$5,200	$5,200
CEM Optical Detector replacement @ $10,000/ea	1/5y						$10,000				
CEM consumables (calibration materials, etc.)	~ $50/week	$2,600	$2,600	$2,600	$2,600	$2,600	$2,600	$2,600	$2,600	$2,600	$2,600
Total Ordinary Operating Cost		$631,800	$631,800	$631,800	$631,800	$631,800	$641,800	$631,800	$631,800	$631,800	$631,800
Total Operating Cost		$749,528	$631,800	$631,800	$631,800	$749,528	$641,800	$631,800	$631,800	$631,800	$749,528
Total Annual Cost		$813,528	$631,800	$631,800	$631,800	$749,528	$641,800	$631,800	$631,800	$631,800	$749,528
Total Life Cycle Cost	$6,745,184										
Present Value of Total Annual Cost (Discount Rate = 3.30%)		$813,528	$611,617	$592,078	$573,164	$658,244	$545,630	$519,969	$503,358	$487,278	$559,609
Present Value of Total Life Cycle Cost (Discount Rate = 3.30%)	$5,864,475										

Table 9. Estimated ten-year life-cycle costs for Scenario 2 Case 3, baseline methods are employed for sampling and analysis of three off gas samples per day, providing near-continuous monitoring only roughly approximating that provided by a CEM.

		Year									
		1	2	3	4	5	6	7	8	9	10
CEM Capital Cost		$0									
Operating Cost											
Trial Burn Cost											
Feed Stream Sampling @$12,000/sample	8 samples	$96,000				$96,000					$96,000
Laboratory Analysis of Feed Stream Samples (for metals) @$366/sample	8 samples	$2,928				$2,928					$2,928
Stack Gas Sampling @ $2000/day	8 days	$16,000				$16,000					$16,000
Laboratory analysis of stack gas samples @$350/sample	8 samples	$2,800				$2,800					$2,800
Total Trial Burn Cost		$117,728				$117,728					$117,728
Ordinary Operating Cost											
Feed Stream Sampling @$12,000/sample	1 sample/week	$624,000	$624,000	$624,000	$624,000	$624,000	$624,000	$624,000	$624,000	$624,000	$624,000
Laboratory Analysis of Feed Stream Samples (for metals) @$366/sample	1 sample/week	$19,032	$19,032	$19,032	$19,032	$19,032	$19,032	$19,032	$19,032	$19,032	$19,032
Stack Gas Sampling @ $2000/day	365 days/y	$730,000	$730,000	$730,000	$730,000	$730,000	$730,000	$730,000	$730,000	$730,000	$730,000
Laboratory analysis of stack gas samples @$350/sample	1095 samples/y	$383,250	$383,250	$383,250	$383,250	$383,250	$383,250	$383,250	$383,250	$383,250	$383,250
CEM technical maintenance service @ $50/hr	~ 0 hr/week	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
CEM Optical Detector replacement @ $10,000/ea	1/5y						$0				
CEM consumables (calibration materials, etc.)	~ $0/week	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Total Ordinary Operating Cost		$1,756,282	$1,756,282	$1,756,282	$1,756,282	$1,756,282	$1,756,282	$1,756,282	$1,756,282	$1,756,282	$1,756,282
Total Operating Cost		$1,874,010	$1,756,282	$1,756,282	$1,756,282	$1,874,010	$1,756,282	$1,756,282	$1,756,282	$1,756,282	$1,874,010
Total Annual Cost		$1,874,010	$1,756,282	$1,756,282	$1,756,282	$1,874,010	$1,756,282	$1,756,282	$1,756,282	$1,756,282	$1,874,010
Total Life Cycle Cost	$17,916,004										
Present Value of Total Annual Cost (Discount Rate = 3.30%)		$1,874,010	$1,700,176	$1,645,863	$1,593,284	$1,645,776	$1,493,113	$1,445,414	$1,399,239	$1,354,540	$1,399,165
Present Value of Total Life Cycle Cost (Discount Rate = 3.30%)	$15,550,580										

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SECTION 6

REGULATORY AND POLICY ISSUES

Regulatory Considerations

There are no regulatory or permitting issues specific to application of the CHRS. When a CHRS-equipped multi-metal CEM is used, the regulatory requirements that pertain to all multi-metal CEMs apply. Initially, those requirements were detailed in the draft performance specification published by EPA (EPA 1996, pp. 17499-17502). When the final rule was promulgated, however, EPA replaced the draft performance specification with performance guidelines that are somewhat less specific and presumably more achievable.

Likewise, there are no worker safety issues specific to CHRS application. When a CHRS-equipped multi-metal CEM is used, the worker safety issues are no different than if the CEM were equipped with a baseline spectrometer. Actually, as compared to the baseline, a CHRS-equipped CEM will likely require less frequent operator attention for maintenance because the CHRS has no moving parts.

As noted earlier, regulatory requirements and costs for trial burns and waste feed characterization are reduced (compared to the baseline) when CEMs are used (regardless of whether the CEMs include a CHRS).

Secondary waste stream regulatory considerations are not affected by CHRS application.

Evaluation of CHRS with Respect to CERCLA Criteria

1. Overall protection of human health and the environment. The implementation of continuous emissions monitoring, enabled by the inclusion of the CHRS in new CEMs, is expected to provide better and continuous control of emissions from thermal treatment of hazardous and mixed waste. Inclusion of the CHRS in new CEMs capable of satisfying EPA performance specifications and the application of those CEMs at mixed waste thermal treatment facilities will permit reduction of feed stream characterization requirements, thus reducing the potential for exposure of samplers and analysts to hazardous and radioactive waste materials.
2. Compliance with ARARs (Applicable or Relevant and Appropriate Requirements). Not applicable.
3. Long term effectiveness and permanence. The improved and more economical characterization and monitoring enabled by use of CHRS-equipped CEMs is expected to provide better knowledge and control of waste treatment processes. This is expected to provide consistently more effective and permanent waste forms.
4. Reduction of toxicity, mobility, or volume through treatment. See item 3, above.
5. Short term effectiveness. The improved and more economical characterization and monitoring of thermal treatment processes enabled by use of CHRS-equipped CEMs is expected to reduce the time (and impacts on human health and the environment) until treatment objectives are achieved.
6. Implementability. The numerous demonstrations and applications of mercury and multi-metal CEMs conducted so far show there is no particular technical difficulty or uncertainty associated with the use of these instruments. Prior to implementation, the performance of CEMs is expected to be verified through the EPA-sponsored Environmental Technology Verification program.
7. Cost. Cost considerations for the CHRS are addressed in Section 5 of this report.
8. State (support agency) acceptance. Technical and administrative issues and concerns the State (support agency) may have are addressed in the preceding subsection of this report.
9. Community acceptance. Positive community reaction is expected because in CEM applications the CHRS provides better and more economical emissions monitoring, thus enabling better control of the waste treatment facilities and complete documentation of operation with respect to emissions.

Safety, Risks, Benefits, and Community Reaction

As noted above, there are no regulatory or permitting issues specific to application of the CHRS. The issues addressed below are those pertaining to the use of CHRS-equipped CEMs.

Worker Safety
- Use of CEMs will minimize worker exposure and hazards associated with the baseline method of providing compliance assurance — trial burn operations and EPA Method 29 sampling and analysis operations.
- As compared to the baseline, use of CEMs will reduce worker exposure associated with feed stream sampling and analysis.

Community Safety and Potential Environmental Impacts
- Use of CEMs will facilitate the control of emissions, thus minimizing the risk of catastrophic releases.
- Compared to baseline operations, implementation of CEMs — and the associated waste feed cutoff provisions — at mixed waste thermal treatment facilities will decrease the likelihood of emissions exceedances and their environmental impacts.

Liability Risk
- CEMs will reduce liability risk by providing continuous data on stack gas emissions at thermal waste treatment facilities. The data can provide proof that the treatment facilities are being operated safely at all times, in full compliance with regulatory requirements.

Potential Socioeconomic Impacts and Community Reaction
- Community reaction is expected to be positive because application of the CHRS in CEMs at thermal waste treatment facilities will provide comprehensive information on stack gas emissions. The baseline approach, stack gas sampling plus off-site laboratory analysis, typically only provides information on emissions during a few hourly periods per year.

Comparison with Baseline and Competing Technologies
- CEM methods will likely be validated through long time use with the reference methods used for compliance monitoring. A record of acceptable performance in this mode of operation will lead to regulatory acceptance.
- Use of CEMs will be perceived as an important improvement over incinerator and HWC validation tests.
- Some stakeholders demand the implementation of CEMs to guarantee operation is within safety and regulatory limits.

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LESSONS LEARNED

Implementation Considerations

The CHRS should be considered in any situation for which high resolution, multi-element sensing capability, and small instrument size/weight are important. Such applications include mercury and multi-element CEM applications.

Technology Limitations and Needs for Future Development

- Sequential bandpass selection. The AOTF bandpass selection is fast and does not involve any moving parts. The currently employed AOTF passes only one wavelength region at a time. Therefore, when monitoring constituents that require m separate AOTF frequency selections, the CHRS is only able to monitor any constituent 1/m th of the time. Higher signal to noise ratios could be achieved if a number of AOTF selection frequencies could be employed simultaneously and each constituent could be monitored for a greater time fraction. Using multiple simultaneous rf driver frequencies, late model AOTFs support simultaneous selection of three separate wavelength regions.
- Wavelength coverage. The AOTF design is optimized for the 200 to 425 nm region. However, this region includes most of the analytical lines of interest for hazardous emissions monitoring.
- Optical quality. Current versions of the CHRS use ordinary spherical optics, so highest quality optical imaging and resolution are not achieved. Higher quality imaging could be achieved if more sophisticated (costly) aspherical optical components were employed.
- Automation. The procedure employed for wavelength calibration of the CHRS could be automated. In that case, the CHRS could be operated entirely under computer control, not even requiring operator intervention for annual wavelength calibration.

Technology Selection Considerations

- Selection of the CHRS is indicated when the advantages unique to it are desired. These include high resolution capability (to avoid interference and/or to achieve increased signal to noise) with extremely fast, non-mechanical wavelength tunability providing multiple analyte measurement capability and real-time background measurement and correction capability. These advantages are needed for the mercury and multi-element CEM applications.
- Site-specific job requirements (specific elements of concern) will influence the technology selection. In particular, the elements of concern will dictate the wavelength regions of concern. One or more of these may fall outside the optimum CHRS performance area.

APPENDIX A

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APPENDIX B

ACRONYMS AND ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
AES	Atomic Emission Spectrometry
AOTF	Acousto-Optic Tunable Filter
ARARs	Applicable or Relevant and Appropriate Requirements
arb.	arbitrary
As	Arsenic
Be	Beryllium
CCD	Charge Coupled Device
Cd	Cadmium
CEM	Continuous Emissions Monitor
CEMS	Continuous Emissions Monitor System
CHRS	Compact High Resolution Spectrometer
Cr	Chromium
CVAAS	Cold Vapor Atomic Absorption Spectrometry
DIAL	Diagnostic Instrumentation and Analysis Laboratory
DOE	U. S. Department of Energy
EM	U. S. Department of Energy Office of Environmental Management
EPA	U. S. Environmental Protection Agency
FPI	Fabry-Perot Interferometer
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
HAP	Hazardous Air Pollutant
Hg	Mercury
HiRIS	High Resolution Interferometric Spectrometer
ICAP	Inductively Coupled Argon Plasma
ICAP-MS	Inductively Coupled Argon Plasma – Mass Spectrometry
ICP	Inductively Coupled Plasma
ICPAES	Inductively Coupled Plasma Atomic Emission Spectrometry
LOD	Limit of Detection
m	meter
MACT	Maximum Achievable Control Technology
MDL	Method Detection Limit
MHz	megahertz
μm	micrometer
n.d.	not detected
n.m.	not measured
nm	nanometer
OST	Office of Science and Technology
Pb	Lead
PDA	Photodiode Array
PMT	Photomultiplier Tube
Pu	Plutonium
rf	radiofrequency
s	second
U	Uranium
UV	Ultraviolet
W	Watt

APPENDIX C

LIMITS OF DETECTION

Part 1 of this appendix provides details concerning limit of detection measurements performed for an air-ICPAES CEM using various CHRS configurations. Part 2 describes proposed CHRS configuration changes and CEM operating procedures and how those changes are expected to provide immediate improvements in the limits of detection.

Part 1.   Limits of detection tests for CHRS-based air ICPAES

Table C-1 details the experimental conditions and measured results from several limits of detection tests for CHRS-based air-ICPAES configurations. As indicated in the table and the associated notes, the experimental configurations included AOTFs from two manufacturers and a 0.2 m monochromator for order-sorting, AOTF drivers from two different sources, and CCD detectors (with single-stage and multiple-stage cooling) from two manufacturers. One AOTF was capable of transmitting one wavelength region at a time; the other was capable of transmitting three separate wavelength regions simultaneously.

Table C-1. Limits of detection (LOD) observed in laboratory and field testing of CHRS-based air-ICPAES systems.

Element and analyte line wavelength (nm)	LOD observed in laboratory testing Sept. 1998 (Baldwin et al. 1998) (µg/dscm)	LOD observed in laboratory testing Nov. 1998 (unpublished) (µg/dscm)	LOD observed in laboratory testing Sept. 1999 (Baldwin et al. 1999) (µg/dscm)	LOD observed in field testing at DIAL Sept. 1999 (Baldwin et al. 1999) (µg/dscm)
Cd 228.80	80	8	1850	150
As 228.81	1640	240	n.m.	n.m.
Hg 253.65	n.m.	80	200	680
Be 313.04	0.5	0.3	0.16	8
Cr 359.35	25	3	12	1.2
Pb 405.78	58	10	80	13
Order sorter	AOTF (Brimrose with Brimrose driver)	0.2 m monochromator	AOTF (MVM Electronics with Ames Lab driver)	0.2 m monochromator
Detector	CCD (Instruments SA)	CCD (Hamamatsu)	CCD (Hamamatsu)	CCD (Hamamatsu)

[a] The LOD values reported for the analytes in stack gas (µg/dscm) were converted from measured LOD values for the analytes in solution (µg/ml). The values were obtained using 1 s measurement times.

The configuration for Column 2 of Table C-1 included an echelle spectrometer with a CCD detector (Instruments SA, Inc., Edison, NJ) and an AOTF (Brimrose Corporation of America, Baltimore, MD) with a Brimrose-supplied RF driver. This AOTF system transmits one wavelength region at a time.

The configuration for Column 3 included an echelle spectrometer with a CCD detector (Hamamatsu, Corp., Bridgewater, NJ) and a 0.2 m monochromator for order sorting.

The configuration for Column 4 included an echelle spectrometer with a CCD detector (Hamamatsu Corp.) and an AOTF (MVM Electronics, Inc., Melbourne, FL) with an Ames Laboratory RF driver. The RF driver had relatively low output power for radio frequencies corresponding to wavelengths less than 235 nm. For those lower wavelengths, the output power was only one-third or less the power output at the other wavelengths. With a proper power supply, LODs for cadmium and arsenic would be expected to improve (decrease) by a factor of at least three. This AOTF can transmit as many as three wavelength regions simultaneously.

The configuration for Column 5 included an echelle spectrometer with a CCD detector (Hamamatsu Corp., Bridgewater, NJ) and a 0.2 m monochromator instead of an AOTF for order sorting. The AOTF crystal scheduled for use in this test did not function properly so the demonstration team used a 0.2 m monochromator in its place. The one week field demonstration schedule did not allow sufficient time for optimization of the optical alignment of the monochromator – echelle combination, however, and the less than optimum performance for cadmium and mercury is attributed to less than optimum optical alignment for the lowest wavelengths. The sample stream was not connected to the DIAL offgas stack and, therefore, was not affected by its pressure variations.

The Hamamatsu CCD detector has single-stage cooling; the ISA CCD detector has multiple stage cooling (lower operating temperature, lower dark current, and lower dark current noise).

Part 2. Limits of detection improvements
Of all the CHRS configurations detailed in Table C-1, the one described in column 4 is most like the target configuration. Its order sorter is based on an AOTF with the ability to transmit multiple wavelength regions so it is capable of providing monitoring that is more continuous than configurations that use an AOTF with single-band transmission and much more continuous than configurations that use a monochromator. As noted earlier, the LODs for Hg, As, and Cd are expected to improve (decrease) by a factor of at least three when the AOTF is operated with an appropriate RF driver. Additional improvements in LODs are expected from a number of other changes:
1. Changing integration time from 1 s to 100 s will improve (decrease) LODs by a factor of 10, i. e., the square root of 100/1.
2. Ray-tracing calculations indicate improvement (decrease) by a factor of two will be achieved by using an off-axis parabolic mirror in place of the present spherical collimating mirror.
3. Use of a CCD detector with multiple stage cooling is expected to reduce dark current and dark current noise and thus yield LOD improvement (decrease) by a factor of two.

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Table C-2 lists the expected improvement factors and the projected LODs, i. e., the LOD values that are expected when all the improvements outlined above are applied.

Table C-2. Projected limits of detection.

Element and analyte line wavelength (nm)	Expected improvement factors	Projected LOD (μg/dscm)
Cd 228.80	1/3, 1/10, 1/2, 1/2	15
As 228.81	1/3, 1/10, 1/2, 1/2	300 [a]
Hg 253.65	1/3, 1/10, 1/2, 1/2	2
Be 313.04	1/10, 1/2, 1/2	0.004
Cr 359.35	1/10, 1/2, 1/2	0.3
Pb 405.78	1/10, 1/2, 1/2	2

[a] This value is based on observations that, for a given concentration, the signal to background ratio and LOD for this As line is usually about 20 times greater than that for the Cd 228.80 nm line.