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Microwave Plasma Metals
Continuous Emissions Monitor Project
Year End Report 1998

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Abstract

Significant progress was made during the past year to develop a sensitive, real-time continuous emissions monitor for accurately measuring a variety of hazardous (Resource Conservation and Recovery Act, RCRA) metals which can be present in the off-gas or stack gas of a thermal treatment process. The current work has focused on six metals: arsenic, beryllium, cadmium, chromium, lead, and mercury. The year started with the analysis of results from a joint DOE/EPA sponsored performance test at the EPA Rotary Kiln Incinerator Simulator Facility at the EPA National Risk Management Laboratory, Research Triangle Park, North Carolina. The majority of the activity during the year has been occupied with laboratory research and development at the MIT Plasma and Science Fusion Center to make performance improvements in the microwave-plasma continuous emissions monitor. The main features of this activity has involved the development and characterization of a fieldable calibration method, experiments with various longer and narrower plasma dimensions, improvements in optics and microwave component configurations, and measurement of plasma parameters to improve understanding of metals emission performance.

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Introduction

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The majority of the activity during the year has been occupied with laboratory research and development at the MIT Plasma and Science Fusion Center to make performance improvements in the microwave-plasma continuous emissions monitor. The main features of this activity has involved the development and characterization of a fieldable calibration method, experiments with various longer and narrower plasma dimensions, improvements in optics and microwave component configurations, and measurement of plasma parameters to improve understanding of metals emission performance. Much progress was made in establishing the real-time calibration technique for aerosols and in improving the detection limits for some of the metals. However much work still remains to be done to reduce calibration error bars and to make additional improvements in the detection limits of mercury and arsenic in air plasmas. This reports summarizes the work that has been done in the past year and the current status of the microwave plasma continuous emissions monitoring technology. More details can be found in publications that were written during the course of the year [1-4] and in one Master Thesis [5]. A number of conference presentations were also given [6-8].

EPA Test Analysis

At the start of the year analysis were completed of the microwave-plasma continuous emissions monitor (MP-CEM) test for trace hazardous metals detection in stack gases at the EPA National Risk Management Laboratory. The initial goal of this test was to demonstrate good measurement accuracy relative to the EPA reference

standard, EPA Method-29.   In this respect the MP-CEM was very successful though only three of the RCRA metals were monitored (Be, Cr, Pb).

This success was accomplished by using an aerosol injection system for injecting a known concentration of metals into the plasma to perform an additive span calibration in the field for the first time. Real-time measurements submitted at the time of the test showed that a relative accuracy of between 20 and 40% was achieved for all the monitored metals for both high ($\sim$ 50 μg/m^3 actual) and low ($\sim$ 15 μg/m^3 actual) concentrations, except for chromium at low concentrations. Results corrected for zero drift after the test, improved the relative accuracy for Be and Pb to about 20%. Corrected chromium results for both high and low concentrations were 43%. These relative accuracy results for the EPA test are summarized in Table 1.

TABLE 1. Relative Accuracies Achieved for EPA Test

Metal	High Concentration	Low Concentration
Lead	20.5%	30.1%
Chromium	42.8%	42.5%
Beryllium	-	16.4%

The chromium discrepancy, and also the small error for lead and beryllium, was found to be systematic. A closer examination of the data suggests that an aluminum tube cold finger between the reference methods and the MP-CEM may have been responsible for much of the discrepancy.   This further suggests that by more careful determination of the span calibration factor, compliance with the EPA goal of 20% relative accuracy may be possible by this approach. However, the work to date has been only with aerosol forms of the metals.

High detection sensitivity in an undiluted stack exhaust plasma was also demonstrated for the three metals monitored. The detection limit, defined as three times the standard deviation of signal noise fluctuations, was shown to depend on the signal integration time. The MP-CEM acquires data very rapidly at up to five times per second. Rapid signal acquisition is an optimum mode of operation for the spectrometer CCD detector arrays to minimize dark current background. Integration of the signals in the software (using 1000 point, 3.5 minute samples for Cr and Pb and a 600 point, 5 minute sample for Be) have shown the detection limit to vary from 50 μg/m^3 for 0.2 seconds to 3 μg/m^3 for 1 minute, respectively. This analysis is shown in Figure 1 where the solid line is a fitted square root plot as predicted for white noise. These results predict that a 1 μg/m^3 detection limit can be achieved for a time resolution of approximately 10 minutes. The results are very encouraging that in future tests the MP-CEM with its attached span calibration subsystem should be capable of achieving EPA's goals for relative accuracy and sensitivity for at least three of the RCRA metals.
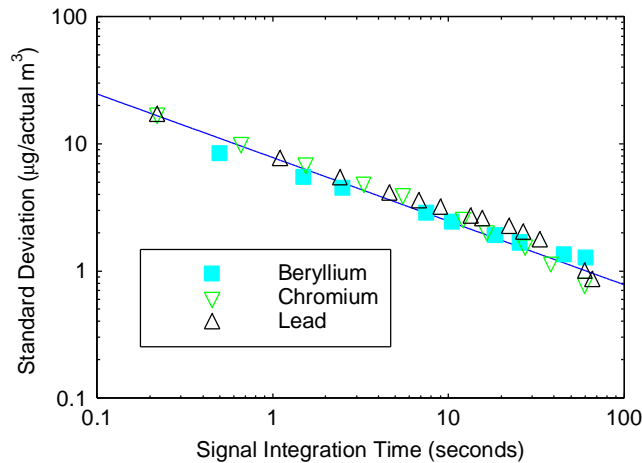
Figure 1. Detection limit (3x vertical axis) as a function of measurement time.

Calibration

A significant effort was made during the year to research and further develop the additive span calibration method tested during the EPA incinerator stack test. This technique uses a pneumatic nebulizer to generate an aerosol containing salts of the metals being monitored, which is then momentarily injected into the stack gas sampling line. The momentary pulse of signal from the span nebulizer is then used to calibrate the response of the MP-CEM to the metals concentration produced by the nebulizer aerosol. Calibrating the MP-CEM is consequently reduced to calibrating the aerosol generation and transport efficiency of the nebulizer system used for the span calibration.

A calibration method of the nebulizer system that could be used in the field while the MP-CEM is fully operational was the focus of much of the experimentation. This calibration method makes a comparison the nebulizer signal for a known uptake rate of a metal solution to a directly inserted known mass of the same metal. The inserted mass is a micro-pipette metered dried droplet, on an alumina rod, of the same solution as that used by the nebulizer. The alumina rod is brought into the plasma vicinity by insertion along the axis of the sample line that transports the stack sample gas and nebulizer aerosol. The alumina rod is not put directly into the plasma generation region. It is only brought close enough to volatilize the metal deposit by the plasma radiation without perturbing the plasma. The perturbation on the aerosol signal by the presence of the rod in the sample line is not large and is corrected for by recording the effect of a blank rod. By comparing the signal from the known directly volatilized mass to the aerosol signal, the nebulizer efficiency can be established.

A lead metals solution was used for most of the measurements. It was found that the nebulizer aerosol generation and transport efficiency determined as described above was a function of the position of the inserted mass sample relative to the plasma. It is important that the directly inserted mass be volatilized as near as possible to the gas sample line termination inside the plasma chamber, so that gas transport efficiency into the plasma excitation region is the same for both the volatilized and aerosol metals. The

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gas sample line is terminated approximately 10 cm upstream from the base of the waveguide within which the plasma is sustained. It was determined that the directly inserted lead must come within at least 5 cm of the waveguide in order for the plasma radiation to be sufficiently intense for complete volatilization with a 1.5 kW plasma. The resulting nebulizer injection efficiencies were in the range of 0.1 - 0.4%. These values did not agree with the measurements carried out at the EPA field test. They were to too low.

In order to position the inserted metals sample further back from plasma and closer to the termination of the sample line, tests were tried with three lower boiling point metals having strong emission lines: strontium (bp 1377 °C), magnesium (bp 1090 °C), and zinc (bp 907 °C). Strong emission signals were readily established with aerosol flows of all these metals. However, in the case of Sr and Zn the blank alumina rods were found to be contaminated with these metals. In the case of Mg a directly inserted signal was not observed.

It was finally found that the best results for these measurements could be achieved by using a tungsten filament for insertion of a known mass of metal deposited on the filament. Inserting the mass on a thin tungsten filament, rather than on the end of an alumina rod allowed boil-off of the inserted mass much further away from the plasma flame due to the smaller thermal inertia of the filament. We were able to go back to using lead again as our calibration metal and to get it to volatilize at up to 8 cm from the plasma. A plot was generated of nebulizer mass transport efficiency versus axial position of the directly inserted mass. As the location of the directly inserted mass was moved further away from the plasma flame, the nebulizer efficiency increased. Linearly extending this plot to the sample line termination provided a determination of the nebulizer aerosol generation and mass transport efficiency of 0.64 ± 0.15 %. This value is 22% lower than that used during the EPA test. Using this value to calculate the relative accuracies for the EPA test would improve the chromium results and slightly degrade the results for lead and beryllium.

Following a midyear review it was recommended that the nebulizer efficiency be checked by a more conventional filter collection method of the aerosol. This method is an accepted laboratory technique for aerosol generation and transport efficiency determinations, but can only be done with the plasma off. Results were obtained using Gelman glass fiber filters to take samples of the span calibration nebulizer output at the sample line termination which would normally be located in the plasma chamber. The microwave waveguide was disconnected for these measurements in order to accommodate a filter with a large surface area. Initially eight filter samples of a lead aerosol flow and one blank were analyzed. Four of the samples were taken with 14 l/min sample gas flow corresponding to the microwave plasma CEM nominal operating condition at the recent EPA field test. And the other four samples were taken with a 42 l/min sample gas flow to test the effect of sample line gas flow on nebulizer aerosol generation and transport efficiency. For the 14 l/min test the resulting nebulizer efficiency was 40% lower than that used for the EPA test. For 42 l/min the resulting

efficiency was 65% lower. Use of either of these values for the EPA test relative accuracy calculations would have produced poorer results.

There was suspicion that some of the aerosol might have blown through the thin Gelman filters. Another ten filter samples were taken and paired with a second filter down stream to collect any aerosol leakage through the first filter. All ten samples were taken at 14 l/min sample flow. The analysis of the ten primary and secondary Gelman filters resulted in a lead transport efficiency of that was even lower, 0.50 ± 0.10 %, than the previous results. The deviation of this result from the earlier value was in the opposite direction from that expected with a second filter to collect more of the aerosol.

Additional measurements revealed that the blow through the glass filters was insignificant. Less than 1% of the lead metal was detected on the secondary. Closer examination of the span nebulizer system suggested that the nebulizer efficiency was changing over the course of the measurements. Sediment was observed in the solution uptake line, which may have built up between the tests and reduced the nebulizer transport efficiency over time.

A new set of three Mienhart pneumatic nebulizers were tested using primary and secondary Gelman filters to collect the lead-containing aerosol. The resulting transport efficiency of lead was in the range of 0.89 – 0.92 % for all three nebulizers. This is in approximate agreement with the original aerosol generation and transport efficiency of the original nebulizer used for the EPA test. A new set of directly inserted lead sample data was also taken with the new nebulizers. The resulting nebulizer efficiencies are somewhat higher than the glass filter results. It is suspected that the linear extrapolation of the direct insertion data to the end of the sample line inside the plasma chamber may be a factor in the disagreement between the direct insertion and glass filter measurements. The tungsten filament will be heated by an electric power source in future measurements to allow injection of the volatilized metal mass exactly at the sample line termination. The new nebulizers will also be monitored over time to determine if there is any degradation in metals transport efficiency with use as suggested by data for the old nebulizer. Eventually additional field testing against EPA-method 29 will be needed to verify the most accurate method for calibrating the span nebulizer.

The linearity of the MP-CEM response to metals concentration was also experimentally checked. The plasma light emission at microwave power levels of 1.0 and 1.5 kW was confirmed to be linear for metals concentrations over a range of approximately 10 to 1000 $\mu g/m^3$ in the input gas flow. The linearity was observed for three different chromium lines at 357.869, 359.349, and 360.533 nm and for lead at 405.707 nm. It is important that signal response be linear over a wide concentration range to facilitate the achievement of accurate measurements in the field, and for laboratory calibration of the span nebulizer.

The experimental results for the chromium 357.869 nm transition are shown in Figure 2. A series of chromium weak acid solutions varying in concentration from 20 μg/ml to 10,000 μg/ml were prepared in steps of 10, 20, 50, etc. Theses solutions were sequentially nebulized into the plasma sample gas flow of 14 l/min and the chromium emission light at 357.869 nm was recorded. Over the solution concentration range from 20 to 2000 μg/ml the emission light was linear as a function of chromium concentration within the experimental error (~ 10%) of the measurements. Above 2000 μg/ml some saturation in the emission light was observed, partly due to the limits of the data acquisition (12 bit A to D). The linear range of solution concentration corresponds approximately to a gas metals concentration range of 10 to 1000 $\mu g/m^3$, of importance to compliance monitoring. The linearity of the plasma response to this range of chromium was the same at 1.5 and 1.0 kW microwave power.
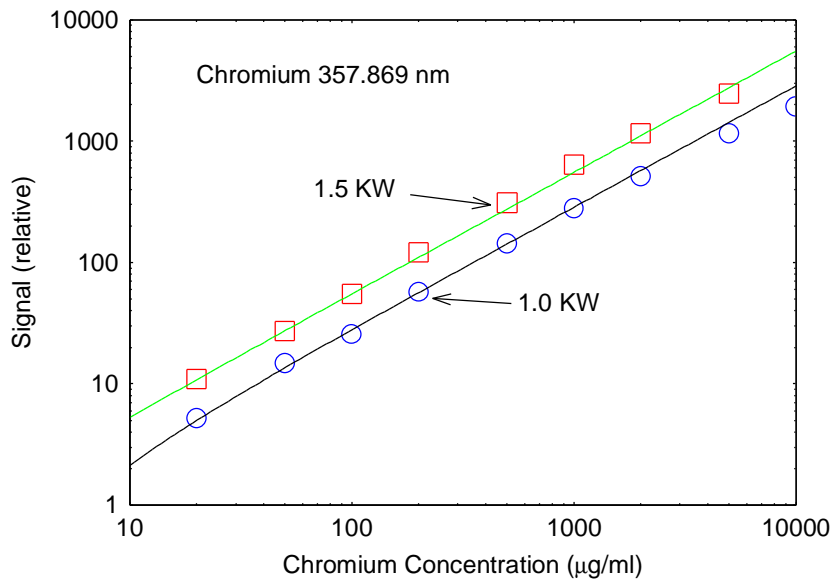

Figure 2. Linear response of the MP-CEM to metals detection.

Hardware and Optics Improvements

A number of plasma hardware and optics modifications were made during the course of the year, which improved reliability of plasma performance and increased the plasma light collection efficiency for spectrometer analysis of trace metals. There were four hardware modifications. The first was to replace the suction pump that draws an isokinetic stack exhaust sample through the plasma with an oil free version of the same pump. During the EPA test the oil mist in the exhaust of the pump was of concern for possibly fouling the exhaust flow meter which was needed to monitor gas flow to insure isokinetic sampling conditions. The second modification was to use a closed water cooling loop for the heat exchanger located between the plasma exhaust and suction pump. The heat exchanger is needed to cool down the plasma exhaust to a temperature that can be tolerated by the suction pump. A closed cooling loop allows use of a

deionized water source in our laboratory without contaminating it and in the field it will allow use of unclean cooling water sources without fouling the heat exchanger. The third modification was the replacement of all the fiberboard gas seals in the hot exhaust gas flow lines with graphite seals. Gas leak rates were noticeable improved. The improved seals reduced suction pumping requirements, are more reliable, and make the determination of sample gas flow easier for calibration. The fourth hardware refinement was that of the wiring harnesses of the two StellarNet detector arrays used in one of our spectrometers. The circuit capacitance was put directly onto the detector chip. This improved detector performance in an electrically noisy environment.

A number of optics experiments and improvements were carried out to increase the UV light collection efficiency of the MP-CEM. In an initial test the fiber optic cable between the plasma and spectrometer was removed and replaced with two UV grade lenses to directly transmit the UV light to the spectrometer. The spectrometer was repositioned directly opposite the lenses on a straight line with the plasma window. A significant improvement in UV light transmission to the spectrometer was achieved. However, the lens coupling of light to the spectrometer, though efficient, was not very rugged because precise and stable alignment was necessary. It also was inconvenient for use with a large spectrometer, requiring lots of space to position the spectrometer input slit on the same axis as the plasma with no flexibility to bring the hardware close together.

An efficient UV fiber optic cable would be much more desirable for transmission of the plasma light to the spectrometer. Careful measurements of UV transmission in our two 1 mm diameter UV-grade fiber optic cables were carried out. At 365 nm the 2 m and 3 m long cables were near 100% efficient, at 228 nm they were 8% and 50% efficient, respectively, and both were completely opaque at 203 nm. Consequently, two new higher-grade fused silica cables were ordered which the manufacturer claimed had an 80% transmission per meter at the 193 nm arsenic line. Tests of the new fiber optic cables showed a significant improvement in UV transmission over the older cables. Experimental comparison between a 1 m long and 2 m long cable having a 0.8 mm diameter core indicate a transmission loss of 40% per meter at 194.23 nm. Direct lens coupling of light to the spectrometer was more efficient, but a short fiber cable could be tolerated for transmission of UV light relevant to arsenic monitoring and allow for more convenient positioning of the spectrometer and plasma hardware components in the field.

Plasma Dimension Modifications

In an attempt to improve metal detection limits, a number of experiments were carried out with modified microwave discharge dimensions. Both longer plasmas to increase metals residence time in the fast flowing gases and smaller diameter plasmas to increase microwave excitation power density were tried. New microwave plasma waveguide components were fabricated for these tests. One set of components modified the plasma excitation region with a path length four times longer than the original system. This was accomplished by putting two full-width WR284 (38 x 76 mm) microwave

waveguides in series along the gas flow direction. The original waveguide was a tapered half width WR284 waveguide. Using the two full width waveguides the microwave excitation path length was increased from 19 mm to 76 mm. Another set of waveguide components in another test decreased the plasma diameter by half from 25.4 to 12.7 mm, which decreased the cross-sectional discharge area by a factor of four.

For the longer discharge configuration stable plasma operation was achieved in both air and nitrogen gas flows with two independent microwave magnetron sources, one each connected to each waveguide. Plasma flame lengths in excess of 9 inches were routinely produced with 800 watts of microwave power per waveguide and with 14 l/min sample gas flow and approximately 5 l/min swirl flow. Increased heat loading of the exhaust gas cooling system was noted and cooling system improvements were made. A more powerful water pump was added to the exhaust heat exchanger system. The exhaust system still ran relatively hot, but several hour operating periods were possible for characterization of metals monitoring sensitivity.

Measurements of the detection limits for mercury, arsenic, cadmium, and lead were carried out for various splittings of the microwave power between the two waveguides. Initial measurements indicated improved detection sensitivities with the longer plasma column using 800 watts per waveguide verses 1.6 kW in one waveguide. However, with more extensive measurements it was found that the detection limits were effected more by the location of the microwave excitation region relative to the light collection optics than by power splitting between the waveguides. The light collection optics have a view along the entire plasma axis, through one waveguide and into the next. There was improvement seen when the microwave power was spilt between the two waveguides versus all the microwave power to the further waveguide, but not when all the microwave power was directed to the nearer waveguide. The closer the microwave excitation region to the light collection optics the lower the detection limits.

The collection optics were subsequently modified from a single lens, which collected light mostly from the afterglow of the nearer waveguide, to a two lens telescope arrangement with a long 8-inch focal length to the inside of the waveguide excitation region. With this optics arrangement the detection limits were shown to be independent of the plasma excitation path length. Apparently the plasma excitation mechanism of trace metals in aerosol form is very rapid inside the microwave waveguide relative to the 14 l/min gas flow speed, such that increasing the microwave excitation path length from 38 mm to 76 mm does not change trace metals detection sensitivity. However, an overall improvement was achieved with the new telescope optics arrangement by more efficient light collection from inside the waveguide excitation region were the trace metals emission is being driven.

A brief test was carried out of the double waveguide system at the maximum 4 kW microwave power available from the two magnetron sources. In this test the suction pump and heat exchanger system were disconnected to avoid possible thermal damage and a pressurized sample gas was blown through the waveguides. Stable plasmas at up to 160 l/min sample gas flow rate (apparently limited only by the maximum available swirl gas flow) were achieved in both nitrogen and air. Microwave power coupling efficiency to the plasma was approximately 94%. The axial viewing optics could not be used due to the very long plasma flame, but side views with a trace aerosol of arsenic did not show a

significant advantage in going from 1.5 to 4 kW for arsenic detection. However, the large flame could be more effective for volatizing larger particles and in highly particulate laden exhaust stacks. The efficient high power microwave plasma torch may also have application to thermal processes for remediating pollution waste steams and in materials processing.

Brief testing was also carried out with a smaller diameter (12.7 mm) plasma to evaluate increased power density for metals excitation. The microwave plasma hardware was converted from a 1-inch to a 0.5-inch diameter discharge tube. A quartz discharge tube was used instead of boron nitride because of on site availability of the smaller size. Initial plasma startup at 1.5 kW mandated exhaust plumbing modifications due to a plasma flame that was much longer than that previously observed with the 1-inch diameter 4 kW plasma discharge. The sample gas flow rate was kept at approximately 14 l/min, but required reoptimization of the sample line diameter down to 4 mm versus the previous 6-mm diameter. A new collection optics lens was implemented with 12-inch focal length, the approximate exhaust flame path length beyond the waveguide, for axial viewing with the telescope lens arrangement. Measurements of the detection limits for mercury, arsenic, cadmium, and lead did not indicated any significant difference from those observed in the 1-inch discharge.

Plasma Measurements and Detection Limits

A number of studies were carried out during the year to better understand plasma performance and plasma parameter relationship to metals sensitivity. These studies included axially integrated rotational and excitation temperature measurements, radial profile measurements, UV transmission measurements, and the effect of gas mixture. Particular emphasis was made on measurements with mercury, cadmium, and arsenic, the three metals that were not monitored during the EPA test. Also considerable attention was given to understanding metals detection performance in air plasmas.

Mercury detection limits, as well as those of cadmium and arsenic, are diminished in air and in oxygen/nitrogen plasmas relative to pure nitrogen or helium discharges. Experimental measurements of mercury emission at 253.65 nm as a function of oxygen addition to pure nitrogen plasmas showed a dramatic drop in mercury emission as oxygen fraction was increased. However, the emission of several iron transitions, which were used for excitation measurements, was significantly increased by the addition of oxygen, opposite to the effect on mercury. Lead emission was also slightly improved with oxygen. Measurements of excitation temperature using trace Fe and Ti metals in the plasma showed that the addition of oxygen decreases plasma excitation temperature slightly by about 10%. Very small fractions of added oxygen (<1%) cause a dramatic decrease in mercury emission and a slight decrease in excitation temperature.

A literature search of electron impact excitation cross-sections for mercury revealed that 5.8 eV electrons are optimum for exciting the 253.65 nm Hg transition and that the excitation cross-section is very sharp on the low energy side. Electrons with energies less than about 4.5 eV would not contribute significantly to exciting mercury at 253.65 nm. The measured air-plasma excitation temperatures, which are sometimes considered to be representative of electron temperature, were in the 0.5 – 1.0 eV range.

This suggests that only the high-energy tail of the electron energy distribution would be effective in exciting mercury. It could therefore be expected that a slight decrease in average electron temperature could indicate a large decrease in high-energy electrons that would cause a correspondingly large decrease Hg emission.

It was also suggested that UV absorption might increase in the plasma with oxygen addition. It is well known that ozone absorbs at 253.65 nm. However, we were able to rule out ozone absorption by low-pressure mercury lamp transmission measurements. Apparently the plasma and adjacent region through which the UV light propagates to our collection optics is too hot for the formation of ozone. Ozone requires temperatures less than 250 °C to form and our plasma exhaust viewing region is hotter than this. However, another UV light absorption mechanism was observed. Transmission measurements with the low-pressure mercury lamp revealed that absorption by unexcited mercury in the outer cooler regions of the plasma gas column is a factor in reducing detection limits for mercury. 253.65-nm transmission measurements along the plasma axis column showed that the added light intensity from the lamp is less when mercury is present in the plasma. This absorption increases with oxygen and is consistent with the interpretation that there is more unexcited mercury in a plasma with oxygen than without oxygen.

To further improve understanding of plasma performance for metals detection, a capability to make radial plasma profile measurements was also developed this year. This was made possible by incorporating a slit in the sidewall of the microwave waveguide to provide a view of the full width of the plasma and by development of a computer code to take an Abel inversion of a series chord measurements along the plasma radial cross-section. The plasma diameter to half-light emission intensity was found to be only be about 10 mm in nitrogen. An Abel inversion of the rotational temperature profiles was obtained in pure nitrogen plasmas where we could get good rotational spectrums of N_2^+. The radial rotational temperature profile in the excitation region inside the waveguide appeared to be flat at about 5400 K over approximately the 10 mm central diameter. This initial Abel inversion temperature profile measurement had poor spatial resolution (~1.5 mm) due to limited fiber optics resolution, which must be improved for future measurements. We hope to exploit this Abel inversion tool for more localized plasma measurements of other emission transitions in the future and thereby gain more insight into the excitation mechanisms of the microwave plasma.

Surveys of possible alternative emission transitions were also made to try to find better lines for detecting mercury, arsenic and cadmium. The greatest success was achieved for cadmium with the discovery of a more sensitive transition in our system at 326.11 nm. The former Cd transition used at 228 nm suffered from much greater self-absorption than the 326 nm line. Also there is preliminary evidence that the 508 nm Cd transition might be better than the 326 nm line. For the case of mercury no transition could be found that was better than the 253 nm line. We examined the 184, 365, and, 404 nm Hg lines. For arsenic all the strong lines are shorter than 200 nm. The strongest As line at 189 nm does not work well in our system primarily due to oxygen absorption and spectrometer inefficiencies. We find that the weaker As lines at 193 and 197 nm perform better. Arsenic has not been studied yet as extensively as the other metals in our system and improvements in the performance of As are expected. Table 2 lists the current status

of the detection limits for 1-minute signal integration times of the six RCRA metals that have been the subject of this year's work. The detection limit is defined as three times the standard deviation of the signal fluctuations.

TABLE 2. 60-second detection limits in air sample gas flow with nitrogen swirl gas

Metal	Transition (nm)	Detection Limit ($\mu g/m^3$)
Pb	405.78	0.3
Cr	359.35	0.6
Be	234.86	0.9
Cd	508.58	6.0
Hg	253.65	12 (2.4*)
As	197.26	144 (9.0*)

* In all nitrogen plasma.

Recommendations for Future Work

Additional improvements are needed in the detection limit performance of mercury, arsenic, and cadmium in air plasmas. On going studies of the plasma performance with Hg and As should continue. Since cadmium is located just above mercury in the periodic table and has the same electronic transitions (the Hg 253 nm and Cd 326 nm transitions are both forbidden triplet-singlet transitions to the ground state) improvements identified by studying mercury should also apply to cadmium. The optimum plasma parameter and excitation region in the plasma for mercury detection should be identified and plasma/optics hardware modifications should be tested to improve those plasma parameters. For example, the recent studies of mercury detection described above suggest that lower electron energies and increased self-absorption are the primary mechanisms that decrease Hg detection limits in the microwave plasma as oxygen is added. Experimentation with plasma hardware modifications that can increase the electric fields to better accelerate the electrons and to decrease the optics viewing path lengths through unexcited plasma regions should be able reduce the detection limits for both mercury and cadmium.

In the case of arsenic extensive studies have yet not been carried out. A key difficulty with As is the very short UV wavelength (<200 nm) of the strong emission lines. Experimentation with improved optics viewing geometries to reduce oxygen absorption in the viewing path lengths and in the spectrometer need to be carried out. A spectrometer better optimized for this UV wavelength region should be tried. Also it may be of value to examine much longer wavelength transition in As at wavelengths > 950 nm. This will require a grating modification in our present spectrometer. Experimentation with improved spectrometers could improve performance for all metals. One test will be to try Dr. David Baldwin's AOTF echelle spectrometer from Ames Laboratory. Also experimentation with very low cost spectrometer components, such as the detector arrays used in the Ocean Optics line of spectrometers, should be continued to develop a low cost multimetals spectrometer that would make possible affordable wide spread use of the MP-CEM.

Calibration development should also continue. Measurements of the fieldable span calibration system need to be followed through to achieve closure between the filter and direct rod insertion calibration methods of the span nebulizer. Possible changes in nebulizer performance with time of use must also be identified. Additional field-testing against EPA method-29 needs to be carried out to further build confidence in this calibration approach. The calibration work to date has also assumed that the calibration nebulizer aerosol of metal salts is representative of all possible exhaust entrained metals forms. This assumption needs to be tested with other forms of metal entertainment such as dry particulate compositions of metals. Particle size limits on calibration need to be measured. Methods for checking zero signal levels in the field must also be developed to allow reliable use of the span calibration signal. The MP-CEM is a promising metals monitoring technology that with additional development could meet the needs for a real-time metals emission monitor in an affordable package.

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