Real-time calibrated microwave plasma multimetals emissions monitor

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ABSTRACT

Real-time calibrated atomic emission spectroscopy in stack exhaust using a continuously sustained microwave plasma is under development for trace metals monitoring. The plasma, in a shorted waveguide attached to the stack by a short sample line, is powered at 1.5 kW, 2.45 GHz. An undiluted stack slipstream is isokinetically directed into the plasma at a nominal flow of 14 liters per minute. A pneumatic nebulizer attached to the sample line can momentarily, on command, inject a known concentration of metals solution providing a real-time calibration. Recent testing has been performed on the exhaust stack of an incinerator at the Environmental Protection Agency (EPA) National Risk Management Laboratory in Research Triangle Park. Three hazardous metals were monitored, lead, chromium, and beryllium. These measurements were referenced to EPA Method-29. A total of twenty spiked stack exhaust tests were carried out. Ten one-hour tests at high concentration (40-60 μg/actual m^3) and ten one and half-hour tests at low concentration (10-15 μg/actual m^3). The microwave plasma monitor achieved measurement accuracies of approximately 20% for lead and beryllium and 40% for chromium with a threshold detection capability of < 3 μg/actual m^3 for a time response of ~1-minute. Laboratory work is continuing to add mercury, arsenic, and cadmium to the monitored metals.

Keywords: microwave plasma, continuous emissions monitor, metals, multimetals, calibration, real-time, stack exhaust

1. INTRODUCTION

Stack emissions of toxic and carcinogenic metals such as mercury, lead, arsenic, chromium, and others pose a serious risk to the environment and the health of the general population. New regulations are being proposed to significantly reduce such emissions from all manufacturing, waste processing, and power production operations. The current standard for metals emission measurements from stationary sources is a sample collection method followed by laboratory analysis[1]. Obtaining results on emissions by this method can take a number of days. The existing measurement standard therefore can only act as a historical record of emissions and is not able to alert operators at the time of an unhealthful metals release to allow immediate corrective action. Compliance with future regulations will require the development of new real-time monitoring instrumentation that is sensitive and accurate.

A number of technologies are under development to meet this need for a continuous real-time metals emissions monitor, including one that is being marketed, described elsewhere in this proceedings[2]. The most common approach of these technologies is to use a plasma for atomic emission spectroscopy (AES). Hot plasmas are ideally suited for real-time metals measurements because they can instantaneously volatilize small particles and droplets, atomize molecular species, and excite the atomic species to emit light for analysis by AES. Therefore the total metals content of stack emissions can be monitored independent of physical form or chemistry. Plasmas have long been used in the laboratory for chemical analysis and can be generated by many techniques[3], most of which are also being tried for the stack emissions monitoring application. These techniques include the inductively coupled plasma (ICP), microwave induced plasma (MIP), laser sparks, and dc electrode spark discharges.

A significant effort has been made to try to adapt laboratory ICP[2, 4-6] and MIP[7, 8] instrumentation. Laboratory instruments have a proven record for sensitive and accurate atomic analysis. They generally operate with very stable, carefully controlled plasma parameters using an argon or helium discharge gas at a slow flow velocity. This mode of plasma operation is not compatible with the isokinetic sampling requirements of stack exhaust, which can be a complex mixture of molecular gases such as water vapor, CO_2, air, etc. at high velocity. Applying laboratory instrumentation to stack real-time monitoring necessitates an elaborate gas-sampling interface between the stack and plasma to slow down the gas velocity, dry it of water, and dilute it with the discharge operating gas. Such a sampling interface can perturb the metals concentration, and can therefore be a potential source of error to measurement accuracy. To overcome this limitation air ICPs are being developed[9-11], but with a consequent decrease in sensitivity and a new challenge to accuracy due to non-ideal and variable plasma

parameters. An air ICP also generally requires over 2 kW of power for stable operation.

Metals monitoring instrumentation making use of laser induced breakdown spectroscopy (LIBS)[12, 13] completely eliminate any gas sampling interface by generating the plasma *in situ* to the stack. However, achieving high sensitivity and accuracy for trace metals analysis in gases has been even more difficult by this approach. Laser breakdown plasmas occur in very small focused volumes in short pulses lasting no more than a few microseconds at pulse repetitions of only a few times per second. Signals must be averaged for many pulses to achieve useful detection limits. Accuracy is effected by shot to shot plasma variations, exhaust inhomogeneities, and the variability with time of the stack exhaust composition. Furthermore, propagation of the UV – optical emission light thorough the stack exhaust and into fiber optics for transmission to a spectrometer represents another variable affecting sensitivity and accuracy. Recent application of *in situ* electrode spark plasmas[14] increases the plasma size and pulse length, but still has the same issues with UV light propagation and accurate calibration.

Recently it has been shown that near *in situ*, stable, moderate power (0.5 – 1.5 kW) microwave plasmas can be generated in undiluted, fast flowing stack exhaust[15]. The sampled stack flow volume is relatively large and continuous, an important consideration for maximizing detection sensitivity and achieving a representative metals content measurement in raw exhaust gases. The plasma is sustained within a standard waveguide with microwave power coupling efficiency approaching 100%. This is in contrast to an ICP, which has a maximum radio frequency (RF) to plasma coupling efficiency of about 50%, the rest of the power being radiated by the induction coils. Working with undiluted stack exhaust presents the same challenge to accuracy as with *in situ* techniques, but by locating the plasma adjacent to the stack, access is possible to actively calibrate metals sensitivity and reduce propagation path lengths for UV light. A microwave plasma device with an aerosol injection system for calibration has been recently tested at the Rotary Kiln Incinerator Simulator facility at the EPA National Risk Management Research Laboratory, Research Triangle Park, North Carolina[16, 17]. Some success was achieved for sensitive and accurate detection of lead, chromium, and beryllium as described below.

2. EQUIPMENT

The major components of the real-time calibrated microwave plasma monitoring system and their configuration are illustrated in Figure 1. A short sample line directs a stack slipstream to the microwave plasma. The sample line has a branch just outside the stack that is connected to a calibration system that can periodically, on command, add a known metal concentration to provide a real-time span calibration. A suction pump system establishes an isokinetic draw of the stack gases into the plasma and returns these gases back to the stack downstream from the sample line. Optics collect the plasma emission light by a longitudinal view down the axis of the plasma column and focus this light onto short fused quartz fiber optic cables for transmission to one or more spectrometers. The spectrometer resolves the atomic emission spectra for detection. Computers identify the relevant metal emission lines and record and display the signal levels in real-time. The calibration system establishes a relationship between the signal levels and the metal concentrations in the plasma.
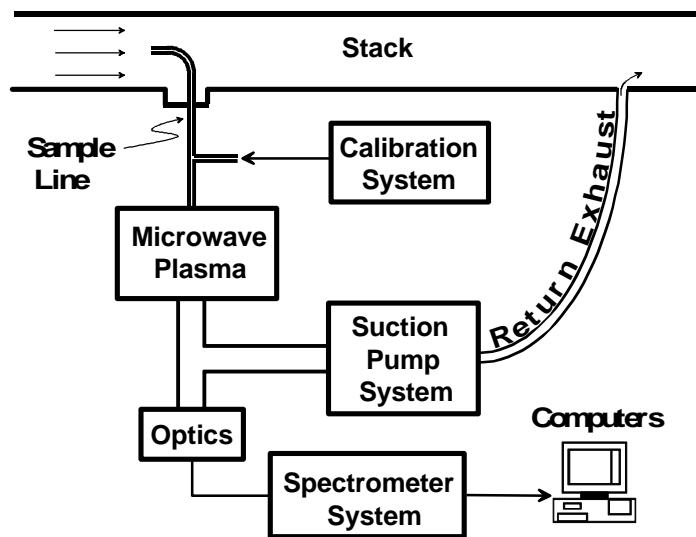

Figure 1. Diagram of major parts of the real-time calibrated microwave plasma metals emissions monitor.

TABLE I. Specifications of major system components.

Component	Description
Microwave generators	1.5 kW, 2.45 GHz magnetron source ASTeX Model S-1500I
	2.5 kW, 2.45 GHz magnetron source ASTeX Model AX2050
Microwave chamber	Shorted WR284 brass waveguide; standard size 38.1 x 76.2 mm and reduced width 19.1 x 76.2 mm
Discharge tube	Boron nitride, 25.4 mm i.d. with 3.18 mm wall
	Fused quartz, 28.6 mm i.d. with 1.59 mm wall
Sample line	Fused quartz, 6 mm i.d. with 1mm wall, 350 mm long to calibration branch
Sample gas flow	14 l/min, nominal
Swirl gas flow	5 – 14 l/min, air, N_2, or other
Calibration	Mienhard pneumatic nebulizer, type A,1 l/min, N_2 with 1 ml/min, nominal, solution uptake with aerosol generation and metals transport efficiency of 0.5 – 1.0%
Calibration solution	Alfa Aesar standard solution with 200 µg/ml concentration each metal
Collection optics	UV grade fused quartz lens 25.4 mm dia., 75 mm focal length
	Above lens with 25.4 mm dia., 200 mm focal length UV lens for telescopic imaging
Fiber Optics	UV grade fused quartz 1.0 and 0.8 mm dia., 1, 2, and 3m lengths
Low resolution spectrometers	Ocean Optics SD1000 dual spectrometer system 1200 groove/mm gratings, 25 µm slits, 1024 element CCD arrays, 190 – 690 nm instantaneous spectral range with ~1.3 nm resolution
High resolution spectrometer, commercial	Instruments SA, Jobin Yvon Spex, Model THR-640, 0.64 m spectrometer with 2400 groove/mm grating, adjustable slit, Princeton Instruments Model IRY-512W intensified 512 element detector array, ~6.5 nm instantaneous spectral range with ~0.05 nm resolution tunable over 180 – 600 nm range
High resolution spectrometer, custom	0.84 m, 3600 groove/mm grating spectrometer, replaceable fixed slits, four 4.5 – 9nm instantaneous bands in 200 – 460 nm range, StellarNet CCD 1,024 and 2,048 detector arrays, best resolution ~0.012 nm

Table I lists the major hardware components and describes their parameters. Two microwave magnetron generators were available and interchangeably used for the experiments. Most measurements were done at a nominal forward power of 1.5 kW. Backward power reflected from the plasma was monitored and could be adjusted to less tan 30 Watts using a triple stub waveguide tuner to match the waveguide impedance between the plasma and magnetron.

Figure 2 shows details of the microwave plasma chamber and discharge tube. In this illustration a tapered waveguide is shown, though standard WR284 waveguide without taper has also been used with slightly higher starting powers. Unlike earlier work with low power MIP devices[7, 8] there is no resonator structure here. The waveguide short facilitates startup, but once started the plasma is sustained by microwave power directly beamed into the plasma without obstruction.   The plasma is initiated by high voltage spark electrodes located at the base of the waveguide. Careful adjustment of these electrodes is necessary to avoid microwave power leakage, but once properly adjusted the microwave leakage meets OSHA regulations for household kitchen ovens.

For most measurements described here, the plasma flame is orientated horizontally. The stack gas to be analyzed for metals content is directed into the plasma chamber by a 6 mm i.d. fused quartz tube at a nominal flow of 14 l/min corresponding to a

stack flow velocity of 8.2 m/s (27 ft/s).   A swirl gas is added in the plasma chamber to keep the plasma off the discharge tube walls. Another gas jet is used to keep the viewing window clean. Both air and nitrogen gases have been used for the swirl and window gases, with the latter preferable for detection of metals with short UV transitions such as mercury and arsenic.
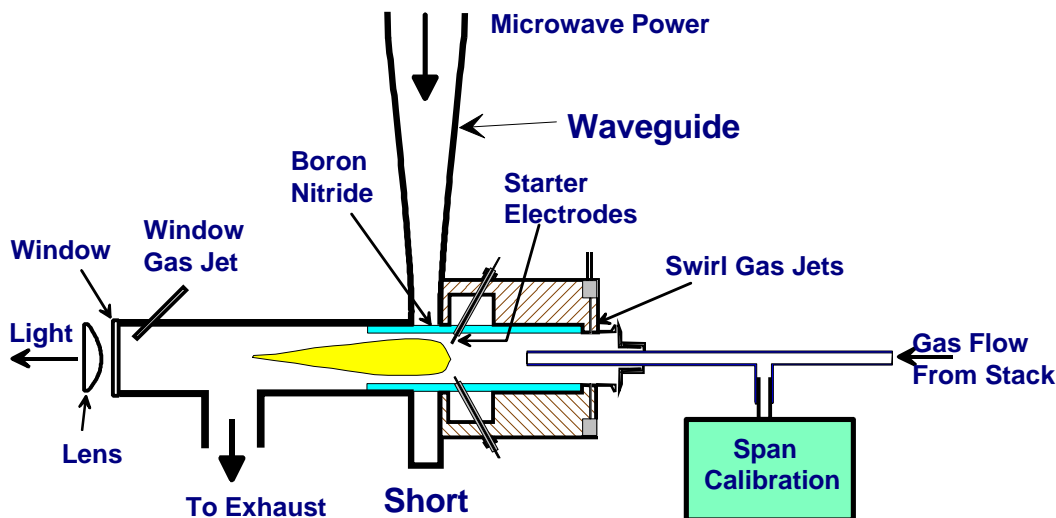
Figure 2. Details of microwave plasma device.

3.   SPECTROSCOPIC MEASUREMENTS

Several spectrometers are used to characterize the plasma and to make quantitative atomic emission measurements.   Low-resolution spectrometers from Ocean Optics were used to survey the background emission spectrum over the entire UV-optical ranged used for metals emission line measurements.   High-resolution spectrometers were used to make plasma temperature measurements and to quantitatively monitor the metals. Initial temperature measurements show a rotational temperature using the N_2^+ molecule in nitrogen plasmas of 5500 ±500 °C and an excitation temperature using atomic Fe emission in air plasmas of 6000 ±500 °C.[18]

Figure 3 shows two background emission spectra over the 190 – 460 nm wavelength range using the low resolution spectrometer. One plot is for both the sample and swirl gases nitrogen and the other for air. The presence of weak NO bands in the nitrogen spectrum suggest that there may be a small air leak into the plasma chamber or an oxygen impurity in the non-laboratory grade nitrogen cylinders. The air spectrum is representative of the kind of background observed when sampling undiluted stack exhaust during the recent EPA field test. A comparison with the spectrum shown by NORE etal[10] suggests that the microwave plasma is hotter than the air ICP by the relative strength of the NO bands to the OH band.

The metal emission line strengths for compliance monitoring are small fractions of the background emission.   The background emission light levels must be subtracted from the plasma spectra in order to detect small concentrations of metals. This is accomplished automatically by the data acquisition software of the high-resolution spectrometers using a stored reference spectrum taken when no metals are present in the plasma. Figure 4 shows high-resolution spectra from 359 to 365 nm taken with the chromium band of the custom MIT spectrometer with a 50 μm slit during the EPA test. The integration time for this spectrum is 0.2 seconds. The top plot is the raw plasma light with the signal from a 92 μg/m^3 concentration of chromium introduced by the span calibration. The chromium transitions are overlapped by rotational transitions from an unidentified background molecular band and are not discernable without subtraction of the background. The bottom plot is the same spectrum with the reference background subtracted.   The chromium lines are evident once the background is subtracted.

The background emission can drift over time from the stored reference spectrum. An additional processing step is therefore made to subtract a representative group of baseline pixels from the detector pixels used for the metal transition.   For

chromium, a group of pixels on an adjacent background transition, illustrated by B in Figure 4, are used to subtract from the signal pixels at S.   For other metals, pixels on either side of the metal transition are averaged for baseline drift correction.
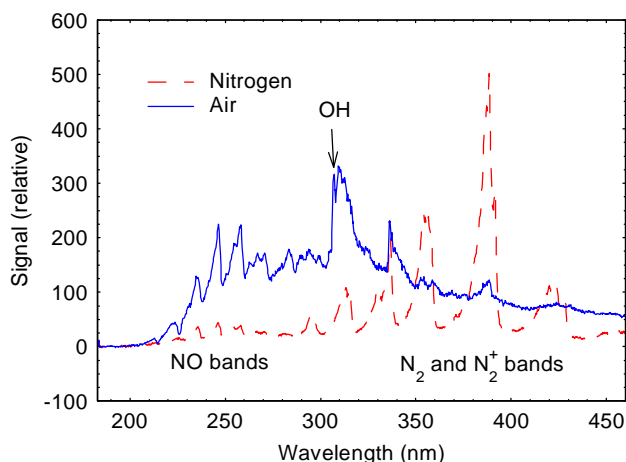

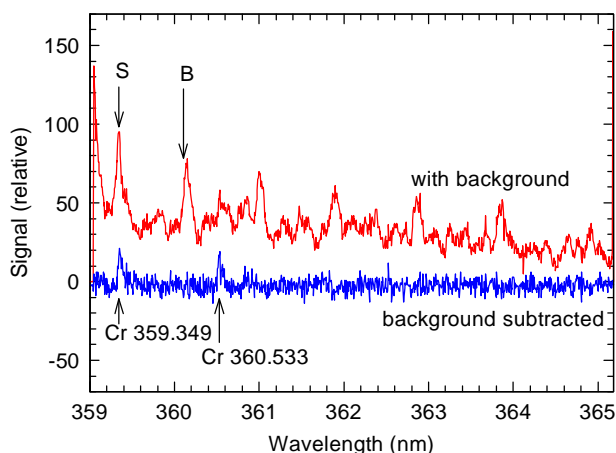Figure 3. Background spectra in air and nitrogen plasmas.

Figure 4. Spectra showing detection of chromium.

4.   CALIBRATION

Real-time span calibration is accomplished by injecting, periodically as needed, a short pulse of an aerosol into the sample line with a known concentration of metals. The span calibration system is connected to the quartz tube tee between the sample probe and the plasma chamber. The major elements of the calibration system are shown in Figure 5. A spray chamber with a Meinhard nebulizer is connected to the branch tube of the tee. A weak nitric acid standard solution prepared by Alfa Aesar containing 200 µg/ml of each metal being quantitatively monitored is delivered by a Masterflex C/L peristalic pump to the liquid input of the nebulizer. The pressurized nitrogen gas flow to the nebulizer is controlled by a MKS Instruments flow controller at a rate of 1 liter per minute. The resulting liquid feed rate into the nebulizer was 1.17 ml/min for the EPA test. Since the nebulizer efficiency for small aerosol droplets that are aspirated into the sample line is very low, most of the standard solution liquid is collected in a waste flask. The tubing connection to the waste flask must be air tight because it is part of the stack vacuum.

The metals concentration injected into the sample line in $\mu g/m^3$ is determined by the formula:

$$C_{span} = e\,\frac{XR}{F} \qquad (1)$$

Figure 5. Span calibration system.

Where ε is the nebulizer efficiency for transport of the metals mass, X is the standard solution concentration in µg/ml, R is the rate of solution pumped in ml/min, and F is the volume flow rate of gas in the sample line in m^3/min.   The solution concentration and pump rate are accurately known as given above. The sample line flow rate is determined by calibrating an exhaust flow meter for sample line suction flow. The nebulizer metal mass transport efficiency is the most difficult parameter to determine in this equation.

Two methods were used for determining ε. In the first, the nebulizer span signal was compared to a directly inserted mass on an alumina rod. A micropipette was used to place a precisely measured 2 to 4 µl droplet of the standard solution on the end of a 4 mm diameter alumina rod. The droplet was allowed to dry and then inserted through the sample line into the plasma
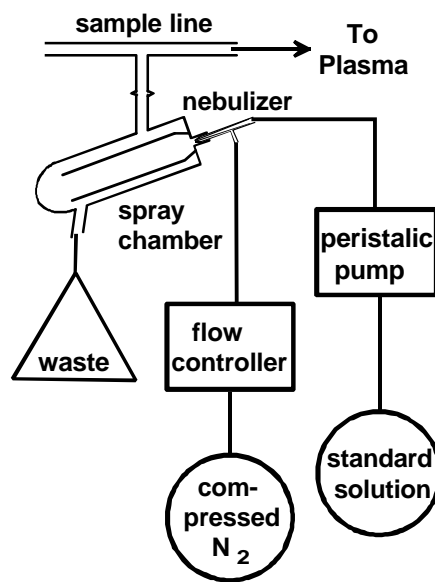
chamber. The tip of the alumina rod with the dried metal sample was not inserted all the way into the plasma, but positioned upstream from the waveguide were the radiated heat from the plasma could vaporize the metal sample. A pulse of signal would result in the appropriate spectrometer detector pixels as the sample was vaporized. Complete vaporization was verified by briefly moving the alumina rod closer to the plasma to confirm that no more metal is detected. The integrated light signal is directly equal to the known metal mass that was deposited on the rod. The nebulizer efficiency is then determined by the ratio of the directly inserted mass to the standard solution up take mass required to produce the same signal. A blank alumina rod was used to account for rod perturbation to the nebulizer aspirated metals signal.

This method of nebulizer calibration has the advantage of being accomplished with the microwave plasma system fully operational at high temperature. However, it was found that the nebulizer efficiency determined in this way depended on the exact position of the rod sample along the axis between the waveguide and end of the sample line. A plot of this dependence was made and extrapolated to the end of the sample line. The resulting nebulizer metals mass transport efficiency determined in this way was $0.64 \pm 0.15\%$ for the nebulizer used at the EPA stack test[19].

A second, more conventional method was also used for nebulizer calibration. Sintered glass filters (Gellman) were used to collect the aspirated nebulizer aerosol at the output end of the sample line and then sent to a commercial laboratory for analysis of the metal content. The microwave plasma chamber and waveguide were disconnected from the sample line for these measurements, but the same suction gas flow was established through the filters as during plasma operation. These nebulizer efficiency results were consistent with the direct rod inserted efficiency determination. Several Mienhard type A pneumatic nebulizers were studied with resulting efficiencies in the 0.5 to 1.0 % range. These measurements are also consistent with earlier studies of this type of pneumatic nebulizer[20].

5. LINEARITY

The rod insertion nebulizer calibration method assumes that the response of the plasma emission light to metals concentration is linear over a wide range of concentrations. As the rod sample is vaporized, the pulse of metals varies from a low concentration to a very high concentration and then back to a low concentration. This integrated light is then compared with a steady low concentration signal from the nebulizer. Measurements with chromium confirmed that the plasma emission light is linear over at least two orders of magnitude of metals concentration. This data is shown in the log-log plot of Figure 6 for two microwave power levels at 1.0 and 1.5 kW. The chromium concentration was varied by using a number of different standard solutions having a chromium concentration from 20 to 1000 µg/ml. This corresponds to a gas flow concentration in the sample line from about 10 µg/m^3 to 5 mg/m^3. The lines through the data points are straight-line fits to the data. Slight deviations from linearity only become evident at the highest concentrations above 2 mg/m^3. The behavior is the same at both 1.0 and 1.5 kW microwave power except that the absolute signal levels are stronger at 1.5 kW.
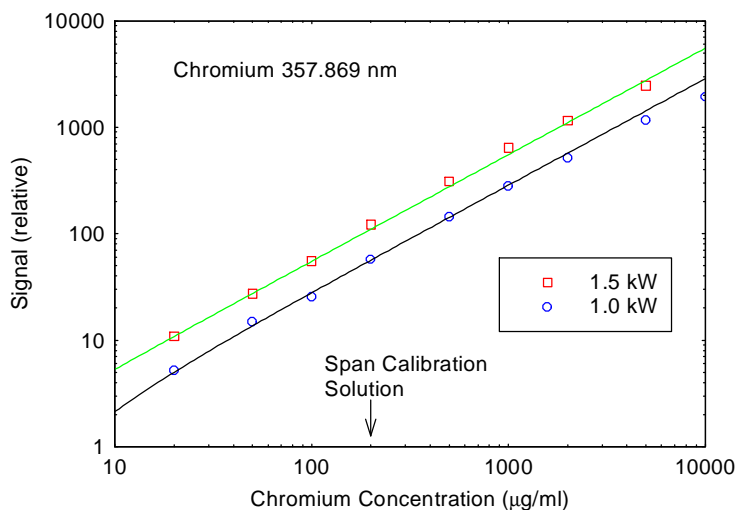

Figure 6. Linear response of chromium emission

6. EPA STACK TEST

The microwave plasma metals emission monitor with its span calibration system was transported to the EPA National Risk Management Research Laboratory, at Research Triangle Park, North Carolina and attached to the exhaust stack of the Rotary Kiln Incinerator Simulator for performance testing. It was one of seven metals monitoring technologies tested on the 20 cm diameter stack[17]. In addition, there were two EPA Method-29 sample collection reference methods operated for relative accuracy determinations. The microwave plasma was the last monitor along the stack going away from the incinerator approximately 7 meters upstream from the nearest EPA reference method.

A series of twenty measurement tests were carried out over a one-week period. Ten tests were at a high metals concentration in the range of 40 – 60 µg/actual m^3 and ten tests at a low concentration of 10 – 15 µg/actual m^3. Six hazardous metals (Hg, Pb, Cr, As, Cd, Be) were introduced into the secondary combustion chamber of the incinerator in an aqueous solution. Also metals containing fly ash was introduced between the primary and secondary combustion chambers. No hazardous materials were burned in the incinerator. The aqueous solution was the primary source of the hazardous metals in the stack while the fly ash contributed some hazardous metals but also mostly a background loading of interfering species such as iron.

The stack exhaust was sampled at a temperature of approximately 400° F and had a water vapor loading of approximately 6.5% mole fraction. The stack gas flow velocity was in the range of 7.6 – 9.1 m/s (25 – 30 ft/s). A 6-mm i.d. fused quartz sample tube intercepted the stack gas flow on axis and directed it into the plasma chamber isokinetically.

The microwave plasma spectrometers were setup to monitor three of the metals (Pb, Cr, and Be) simultaneously. The other three metals were still under development to improve sensitivity at the time of the EPA test. Signals were acquired five times per second for Pb and Cr, and twice a second for Be. The displayed and recorded signal for each metal was corrected for background light and baseline drift in real-time as described in Section 3 above. Figure 8 illustrates how the monitored metal signals looked by showing the Pb and Cr data for the ninth high concentration test. The data shown has been smoothed with a 6-second integration time constant.
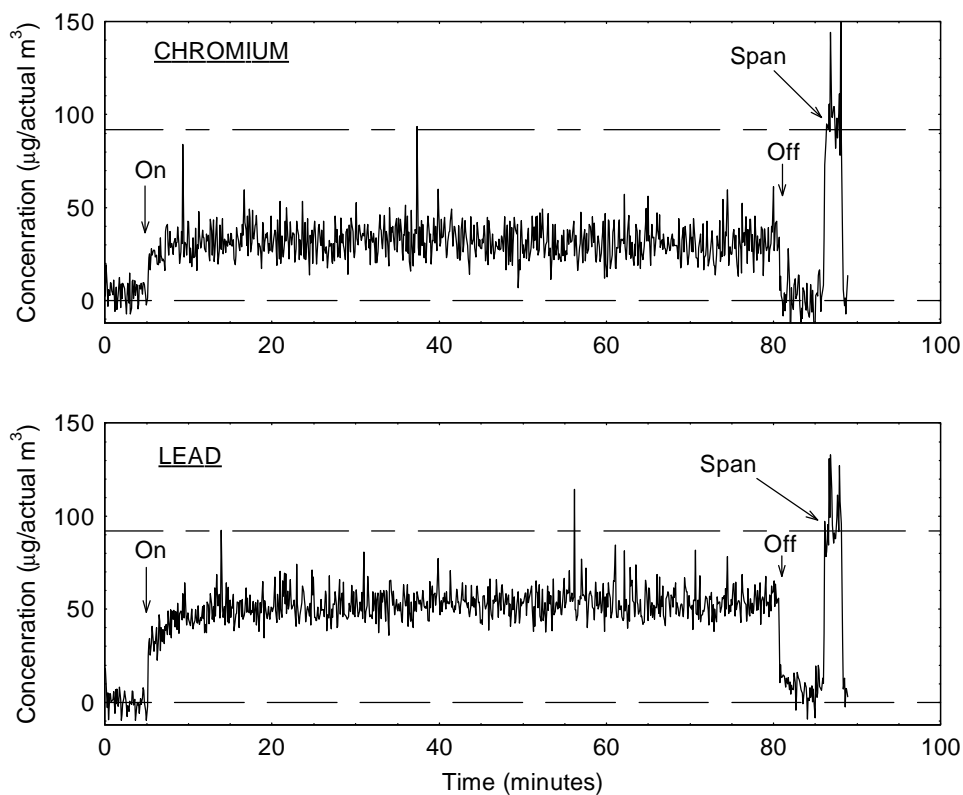

Figure 7. Chromium and lead real-time signals for ninth high-concentration stack test.

A typical test would start with the turn on of the aqueous metals feed to the incinerator. A sudden jump in the metals signal levels would be observed as indicated by the "on" arrow in Figure 7. The metals feed would remain on for a little over one hour for each high concentration test and a little over an hour and a half for the low concentration tests to give the EPA reference methods enough time to collect measurable samples. At turn off of the aqueous metals feed a sudden drop in metals signals would occur as shown by the "off" arrow. The span calibration aerosol would be turned on for a 1-2 minute period after the aqueous metals feed was turned off. The vertical scale of the plots in Figure 7 were set by this span signal, which corresponded to 92 µg/m^3 metals concentration. The span signal could be turned on before the metals feed, during it, and/or after the metals feed as shown in Figure 7.

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The fly ash feed was on continuously throughout the test period and not turned off and on with the aqueous metals feed. At the 0.2-second time resolution occasional fly ash signal transients exceeded the average aqueous metals feed signal levels by one to two orders of magnitude. For the 6-second smoothing of the data shown in Figure 8 most of these fly ash transients have been averaged out. However, a few traces are still seen including some structure on the span signal. The fly ash did not contribute significantly to the averaged hazardous metals signals.

The averaged microwave plasma measurements are compared to the average of the two EPA reference measurements in Table II. The metals concentrations have been converted to dry standard cubic meters by the formula

$$C_{dry} = C_{act} \frac{100}{(100-M)} \frac{(273+T)}{293} \qquad (2)$$

were C_{act} is the concentration in actual cubic meters, M is the mole per cent of water in the exhaust, and T is the temperature of the exhaust in degrees centigrade. Most of the missing entries in Table II are due to software data losses, which was not fully debugged in time for this field test. Table II contains a few more microwave plasma entries than the original report[17] due to additional data recovery. Also, some of the results differ because a correction has been made for zero drift between the start of metals feed and the end of metals feed in tests were such drift was noticeable.

TABLE II. Stack measurement results for the microwave plasma (MP) and the EPA reference method (EPA) in μg/dry standard m^3

Test #	Lead		Chromium		Beryllium	
	MP	EPA	MP	EPA	MP	EPA
1	75.0	93.4	35.0	71.7		
2	75.8	52.2	53.8	44.9		
3	63.7	74.7	44.9	64.2		
4	69.0	67.1	45.0	56.2	57.5	54.3
5	78.1	42.0	48.5	40.0		
6	61.4	93.2	37.4	68.7		
7	-	95.3	-	71.9		
8	95.4	93.2	49.0	70.0		
9	94.3	91.8	57.2	70.8		
10	71.9	78.8	47.3	63.1		
11	15.4	27.8	16.6	28.8	13.5	19.3
12	19.6	23.3	20.2	24.8	-	16.0
13	19.5	20.2	13.0	22.2	14.9	14.9
14	15.9	26.0	20.4	27.6	16.0	18.8
15	22.6	27.8	21.5	31.3	16.6	19.5
16	22.8	30.9			24.2	22.2
17	26.1	29.4			28.2	23.1
18	25.9	31.5			23.4	23.5
19	26.6	29.5	19.4	29.3	19.9	21.3
20	20.0	23.5			16.1	17.4

The general agreement between the microwave plasma and the EPA reference method is fairly good for a first time field test of this particular metals monitoring technology. Of the 44 individual tests listed in Table II all but two agree within 50%. More than two thirds of the measurements for lead and beryllium are within 20% and many are within 10%. Chromium shows a systematic offset of 20 – 50% to lower concentrations and the small error of the other metals is also on average to lower values. It is possible that an intervening cold probe in the stack between the microwave plasma and the EPA reference methods could have perturbed the metals concentration downward[16].

7. RELATIVE ACCURACY

A procedure for calculating the relative accuracy of a multimetals continuous emissions monitor (CEM) to the EPA reference method has been specified by the EPA[21].   The equation used to make the comparison is

$$RA = \frac{\left|\bar{d}\right| + \frac{t_{0.975}}{\sqrt{n}}(SD)}{\bar{R}_{RM}} \tag{3}$$

where $\bar{d}$ is the mean of the differences between the CEM and reference method, SD is the standard deviation of $\bar{d}$, n is the number of measurements, $\bar{R}_{RM}$ is the average of the reference measurements, and $t_{0.975}$ is the t-value confidence error as given in Table III. Equation (3) was evaluated for the above data and the results are given in Table IV. For lead and beryllium the relative accuracies are at or close to the EPA goal of 20%. For chromium the error is larger, but it is systematic and not random. If the span calibration were decreased by 30% then the chromium relative accuracy would be improved to about 20% also. A small decrease in the span calibration would also improve the relative accuracies of lead and beryllium.

TABLE III. t-values

n	$t_{0.975}$
2	12.706
3	4.303
4	3.182
5	2.776
6	2.571
7	2.447
8	2.365
9	2.306
10	2.262
11	2.228
12	2.201

These results suggest that the EPA goal of 20% relative accuracy to the current reference method can be achieved. They also suggest a method by which this can be accomplished reliably, by calibrating the span nebulizer with the EPA reference method.   Such a calibration method would tend to compensate the span aerosol signal for variables due to different forms of metals in the stack. It would also directly tie the real-time measurements to the currently accepted standards.

TABLE IV. Relative Accuracies

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

8. DETECTION LIMITS

Sensitivity of a multimetals emissions monitor is given in terms of the detection limit. Detection limit is generally defined as a metal concentration which yields a signal that is equal to three times the standard deviation of the signal noise fluctuations. The standard deviation for a given data set is a measure of how precisely a root mean square (rms) value can be assigned to that data set. For thermal or white noise, the standard deviation varies as the inverse square root of the signal integration time. Incoherent plasma light emission is inherently a thermal process. Therefore, detection limit and measurement time are related to each other. The lower the detection limit, the longer will be the measurement time and instrument response time.

The detection limit and its relation to the measurement time were evaluated for the data taken during the EPA test. Figure 8 shows the analysis of the signal fluctuations for the three metals monitored by the microwave plasma. For chromium and lead, 3.5 minute data sets of approximately 1000 points each were evaluated over a period when the signal level was relatively flat with fly ash on but no metals feed. For beryllium, a 5 minute time period of 600 points was evaluated with both fly ash and metals feed.   Each of the data sets was filtered with a number of different integration times, covering the range from 0.2 seconds to 1 minute for Cr and Pb, and 0.5 seconds to 1 minute for Be. For each integration time, the standard deviation of the resulting data set was calculated and plotted in Figure 8. The straight line on the log-log plot is the best fit of a square root function to all the data points. There is good agreement for a white noise relationship between the standard deviation and the integration time and no evidence of a 1/F noise limit out to the maximum one minute integration time considered here. Taking three times the standard deviation as the detection limit, the present microwave plasma results show that for an integration time of 0.2 seconds the detection limit is approximately 50 $\mu g/m^3$. At one minute it decreases to approximately 3 $\mu g/m^3$, and it is projected to be 1 $\mu g/m^3$ for an integration (measurement) time of approximately 10 minutes.
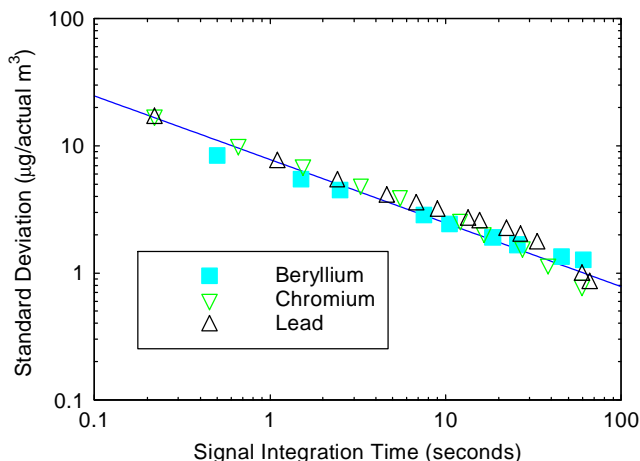
Figure 8. Detection limit (3x vertical axis) as a function of measurement time.
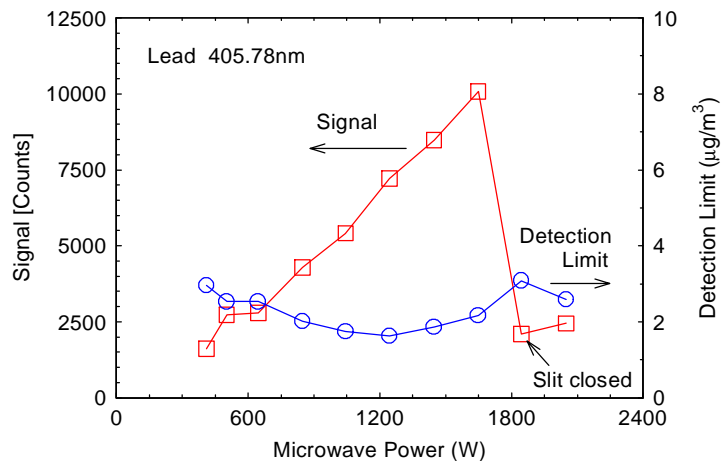
Figure 9. Signal strength and 40-second detection limit dependence on microwave power.

The effect of microwave power on the detection limit was also examined in laboratory air plasmas after the EPA field test. It was well known that the absolute light emission strengths of the metal transitions increase with power. Figure 9 shows a study of lead emission over a microwave power range from 400 to 2000 watts documenting this effect. The emission line strength increases so much with power that at 1650 watts the ISA spectrometer slit width was reduced to prevent detector saturation. However, the standard deviation of the signal also increased with power so that the detection limit was approximately constant over this power range at 2-3 $\mu g/m^3$ for 40-second time resolutions as shown by the lower curve. This result suggests that high power microwave sources are not necessary for sensitive detection, but high power microwaves would still be important in applications were robust plasma operation is required in the presence of particle and water vapor loadings in the stack gas.

Table V summarizes the current detection limit status of the real-time calibrated microwave plasma metals emissions monitor for the six metals that were the subject of the EPA field test. Very good sensitivity exists for Pb, Cr, and Be as demonstrated in the field test. Cadmium has useful sensitivity and shows promise of improvement. Arsenic and mercury have the poorest sensitivity to date. Working with air plasmas causes the greatest challenge for their detection. The detection limit for these metals is much lower in pure nitrogen plasmas, but the addition of a small amount of oxygen degrades their performance. In the case of mercury this may be due to a slight cooling of the electron temperature. In the case of arsenic it is probably due to increased absorption of the short wavelength UV light. Studies are continuing in the laboratory to better understand the performance of mercury and arsenic in air plasmas and hopefully to make improvements.

Table VI. 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	1.2
Cr	359.35	2.4
Be	234.86	3.6
Cd	508.58	20
Hg	253.65	92 (17*)
As	197.26	144 (35*)

* In all nitrogen plasma.

9. CONCLUSIONS

The real-time calibrated microwave plasma metals emissions monitor has shown significant promise for meeting the hazardous metals monitoring requirements being considered by the EPA for a multimetal CEM. Both high sensitivity and good accuracy have been demonstrated in the first field test of this technology. The microwave plasma hardware is compact, robust, and makes use of readily available and inexpensive microwave components. Unlike earlier low power MIP devices no resonator structure is used or required to sustain the plasma. Microwave power is beamed directly into the plasma in a

standard waveguide without obstructions. Power coupling efficiency into the plasma approaches 100%. In comparison to an air ICP it can be operated stably in air at much lower power levels, more efficiently, and apparently with a hotter plasma temperature. There is no microwave power radiated or leaked from the plasma when properly assembled. In comparison to *in situ* spark discharges it is a continuous plasma with a 100% duty factor exciting plasma volumes per second many orders of magnitude larger. By being near *in situ* just outside of the main stack exhaust flow, the plasma is accessible for calibration and is also nearer to UV spectrometers for more efficient UV light collection. It should therefore be inherently more sensitive and accurate to trace metals monitoring. The microwave plasma technology as described here also has a unique rapid time response capability. This feature could provide insights into plant operations such as demonstrated by turn on and off of metals spiking in the EPA stack test. Given additional maturing of this technology it should be capable of meeting the real-time metals monitoring goals as presently envisioned by the EPA.

10. ACKNOWLEDGEMENTS

11. REFERENCES

1. Environmental Protection Agency, EPA Stationary Source Sampling Methods, EPA Method-29, Rev. 2, 6/94.
2. G. A. Meyer, "Real-time analysis of metals in stack gas using argon/air ICP optical emission spectrometry" this proceedings, 1998.
3. M. W. Blades, P. Blanks, C. Gill, D. Huang, C. Le Blanc, and D. Liang, "Application of weakly ionized plasmas for materials sampling and analysis", *IEEE Trans. on Plasma Sci.* **19**, pp.1090-1113, 1991.
4. C. Trassy, R. Diemiaszonek, P. Pasquini, and R. Meunier, "On-line analysis of elemental pollutants in gaseous, effluents by inductively coupled plasma-optical emission spectroscopy", *Proc. of the International Sym. on Environmental Technologies: Plasma Systems and Applications, pp. 401-408, Atlanta, Oct. 1995.*
5. G. A. Meyer, K. W. Lee, "Real-time determination of metal hazardous air pollutants in flue gas emissions: laboratory study", *Process Control and Quality*, **6**, pp.187-194, 1994.
6. M. D. Seltzer, R. B. Green, "Instrumentation for continuous emissions monitoring of airborne metals", *Process Control and Quality*, **6**, pp.37-46, 1994.
7. V. Siemens, T. Harju, T. Laitinen, K. Larajava, J. A. C. Brokaert, "Applicability of microwave induced plasma optical emission spectrometry, (MIP-OES) for continuous monitoring of mercury in flue gases", *Fresenius J Analytical Chemistry*, **351**, pp. 11-18, 1995.
8. J. F. Camuna-Aguilar, R. Pereiro-Garcia, J. E. S⟨nchez-Uria, and A. Sanz-Medel, "A comparative study of three microwave induced plasma sources for atomic emission spectrometry—I. Excitation of mercury and its determination after on-line continuous cold vapour generation" *Spectrochimica Acta*, **49B**, pp. 475-484, 1994.
9. D. P. Baldwin, D. S. Zamzow, and A. P. D'Silva, "Detection limits for hazardous and radioactive elements in airborne aerosols, using inductively coupled air plasma – atomic emission spectrometry", *J. Air & Waste Manage. Assoc.*, **45**, pp. 789-791, 1995.
10. D. Nore, A. M. Gomes, J. Bacri, and J. Cabe, "Development of an apparatus for the detection and measurement of the metallic aerosol concentrations in atmospheric air *in situ* and in real time: preliminary results", *Spectrochimica Acta*, **48B**, pp. 1411-1419, 1993.
11. D. P.Baldwin, D. S. Zamzow, G. P. Miller, "AOTF-Echelle spectrometer for air-ICPAES continuous monitoring of heavy metals and actinides", this proceedings, 1998.
12. D. W. Hahn, "Laser - induced breakdown spectroscopy for sizing and elemental analysis of discrete aerosol particles", *Applied Physics Letters*, **72**, pp. 2960-2, 1998.
13. J. P. Singh, Fang-Yu Yueh, Hansheng Zhang, R. L. Cook, "Study of laser induced breakdown spectroscopy as a process monitor and control tool for hazardous waste remediation", *Process Control & Quality*, **10**, pp.247-58, 1997.
14. M. E. Fraser, A. J. R. Hunter, S. J. Davis, "Real-time monitoring of airborne metals", this proceedings, 1998.
15. P. P. Woskov, D. Y. Rhee, P. Thomas, D. R. Cohn, J. E. Surma, C. H. Titus, "Microwave plasma continuous emissions monitor for trace-metals in furnace exhaust", *Rev. Sci. Instrum.*, **67**, pp. 3700-3707, 1996.
16. Paul P. Woskov, Kamal Haddidi, Paul Thomas, Karyn Green, Guadalupe Flores, and David A. Lamar, "Field Test of a Real-Time Calibrated Microwave Plasma Continuous Emissions Monitor for Stack Exhaust Metals", MIT Plasma

Science and Fusion Center, PSFC/RR-98-1, 1998.

17. 1997 Performance Testing of Multi-Metal Continuous Emissions Monitors, U. S. DOE and EPA report, to be published , 1998.

18. P. P. Woskov, K. Hadidi, M. C. Borrás, P. Thomas, K. Green, G. J. Flores, "Spectroscopic Diagnostics of an Atmospheric Microwave Plasma for Monitoring Metals Pollution", *Rev. Sci. Instrum*, **70**, to be published, 1999.

19. G. J. Flores, "Establishing a Calibration for a Microwave Plasma Continuous Emissions Monitor", Master Thesis, MIT, Cambridge, Massachusetts, 1998.

20. D. D. Smith and R. F. Browner, "Measurement of Aerosol Transport Efficiency in Atomic Spectrometry", *Analytical Chemistry*, **54**, pp. 533-537, 1982.

21. U. S. EPA, Revised Standards for Hazardous Waste Combusters, Performance Specification 10 – Specifications and test procedures for multimetals continuous monitoring systems in stationary sources, 61 FR 17499 –17502, April 19, 1996.