

ACCURATE AND SENSITIVE METALS EMISSIONS MONITORING WITH AN ATMOSPHERIC MICROWAVE-PLASMA HAVING A REAL-TIME SPAN CALIBRATION

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ABSTRACT

Both high sensitivity and good measurement accuracy are required in a metals continuous emissions monitor in order for it to be acceptable for compliance monitoring. An atmospheric plasma sustained by microwaves with an attached source of a calibrated trace metals aerosol has been shown to be capable of achieving both of these requirements. The microwave plasma is continuous and operates in undiluted stack exhaust for atomic emission spectroscopy of trace metals. The plasma is sustained in a shorted waveguide that is attached to the stack by a short sample line (< 50 cm). It is powered at 1.5 kW, at a frequency of 2.45 GHz. An undiluted stack slipstream is isokinetically drawn into the plasma by a suction pump at a nominal flow of 14 liters per minute. The pneumatic nebulizer attached to the sample line can momentarily, on command, inject a known concentration of metals solution providing a real-time span calibration. The system was tested on the exhaust stack of the rotary kiln incinerator simulator facility 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 $\mu\text{g}/\text{actual m}^3$) and ten one and half-hour tests at low concentration (10-15 $\mu\text{g}/\text{actual m}^3$). The microwave plasma monitor achieved relative accuracies of approximately 20% for lead and beryllium and 40% for chromium with a threshold detection capability of < 3 $\mu\text{g}/\text{actual m}^3$ for a time response of ~1-minute. The relative accuracy deviation from the EPA Method-29 was found to be mostly systematic. This suggests the possibility of using a site-specific calibration to bring the microwave plasma into compliance with EPA's goal of 20% relative accuracy to the reference method. Laboratory work is continuing to add mercury, arsenic, and cadmium to the monitored metals. Mercury and arsenic present a particular challenge to achieving high detection sensitivity in undiluted stack exhaust because the plasma is less efficient in exciting Hg and because UV absorption interferes with As detection. This is a problem that is also in common with air ICP and *in situ* spark plasma methods for continuous emissions monitoring of metals.

INTRODUCTION

Advancing the state-of-the-art of continuous emissions monitoring (CEM) technology for rapid and simultaneous detection of all hazardous metals in stack exhaust is currently the focus of significant development activity. Such a CEM must be able to monitor at a minimum six of the Resource Conservation and Recovery Act (RCRA) metals: arsenic, beryllium, cadmium, chromium, lead, and mercury. Detection limits on the order of $1\mu\text{g}/\text{m}^3$ are needed with minimum accuracies of 20% relative to the current Environmental Protection Agency (EPA) reference method. In addition, the goal is to develop an instrument that is affordable, easy to use, low maintenance, and user safe.

Meeting all of these requirements in a single CEM instrument is a significant challenge. The most promising approaches make use of a plasma for atomic emission spectroscopy (AES). A high temperature plasma generated in the stack or in a continuously drawn sample from the stack can atomize and excite metals that are adsorbed in fine particulates, bound in molecular species, or are unspiciated. Thus total metal content independent of chemical or physical form can be comprehensively monitored in real-time by passing the stack gas through the plasma state.

The utility of using plasmas for elemental chemical analysis has been known for several decades. Inductively coupled plasmas (ICPs), microwave induced plasmas (MIPs), dc and ac electrode discharges, and other plasma sources are used in many commercially available laboratory instruments for analytical spectrochemistry [1]. Adapting laboratory plasma sources to stack analysis requires a sophisticated gas-

sampling interface with the stack. This is necessary because laboratory instruments are generally designed to operate with argon gas and prepared samples that are introduced into the plasma with very slow flow velocity. A number of tests have been carried out with commercial ICPs for this application [2-4] and the first commercially available CEM for metals is based on this approach [5].

Most other metal CEM development is focused on using a plasma generation method that is compatible with the stack gas composition and environment to significantly simplify, or completely eliminate, the need for a sophisticated gas sampling interface. These plasma generation methods include air ICPs [6-8], an undiluted stack gas microwave plasma [9], laser sparks [10,11], and dc electrode spark discharges [12]. Each of these plasma generation methods has its particular advantages and disadvantages, but a common problem is achieving and maintaining an accurate calibration of the trace metals measurements under variable gas matrix and stack environment conditions. The calibration can change due to changing exhaust chemistry, variable particle loading, deposition of films on windows, temperature drifts of electronics, drifts in optics alignment, and other variables in the field environment of a stack exhaust. Also some metals such as mercury and arsenic have higher detection limits in a stack exhaust plasma due to reduced atomic excitation efficiency [13], increased self absorption, and/or UV absorption by other species such as oxygen and related molecules.

To achieve acceptable metals concentration measurement accuracies for compliance measurements, it is necessary that a stack mounted metals CEM be capable of self-calibration during operation. Also to minimize detection limits it should be designed with the shortest possible UV propagation path lengths through unexcited stack gases. In the present work we show that a large volume, continuous microwave discharge sustained in a stack slipstream with an attached span calibration system can achieve measurement accuracies within 20%. It can also have certain advantages for lower detection limits and more efficient operation relative to other stack mounted CEMs.

HARDWARE

The main hardware elements of microwave plasma (MP) CEM system with an attached span calibration are shown in Figure 1. A short sample line (< 50 cm), which in the present system is a 6-mm i. d. quartz tube, intercepts the exhaust flow in the center of the stack and directs this flow to the plasma. A branch in the sample line just outside the stack connects to a calibration system that can periodically, on command, inject a known metal concentration for real-time span calibration. The stack gas sample is drawn isokinetically by a suction pump, which returns these gases, after analysis, to the stack downstream of the sample line. The plasma emission light for AES is viewed with UV grade optics along the axis of the plasma column for most metals, but can also be viewed radially for those metals for which the propagation path lengths through unexcited stack gas must be kept to a minimum. Short fiber optic cables transmit the light to one or more spectrometers that resolve the atomic emission spectra for detection. Computers process the light signal for background interference, 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 as often as necessary.

The specifications of the major hardware components of the MP-CEM are listed in Table I. The nominal microwave power used for most measurements is 1.5 kW, though stable plasmas in air have been operated at power levels less than 0.5 kW and up to 2.5 kW with a single microwave source. Detectors built into the microwave sources monitor forward and backward transmitted microwave power. Reflected power can be adjusted with a triple stub tuner for matching the impedance of the plasma to the magnetron source to less than 2%. Consequently, the coupling efficiency of the microwaves to the plasma approaches 100% which is in sharp contrast to the best RF coupling efficiencies of approximately 50% for air ICPs.

The details of the microwave plasma chamber and discharge tube are shown in Figure 2. The plasma is sustained inside a shorted waveguide, which is a standard WR284 waveguide having an outer cross-section of 3 by 1.5 inches or, as shown in Figure 2, a tapered guide with 3 by 0.75 inch cross-section. Unlike earlier work with low power microwave induced plasma (MIP) devices, 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. High voltage spark electrodes located at the base of

the waveguide initiate the plasma. Careful adjustment of these electrodes is necessary to avoid microwave

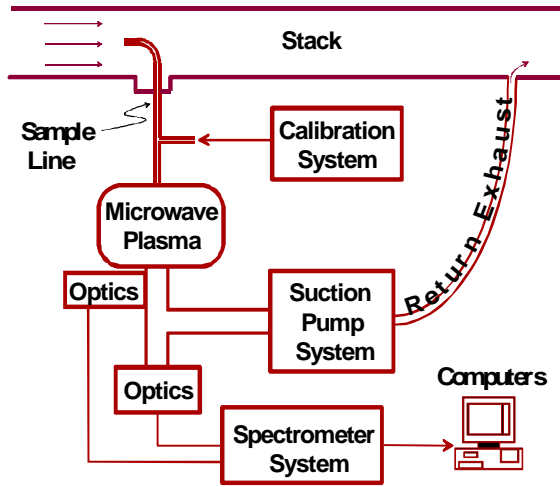


Figure 1. MP-CEM system

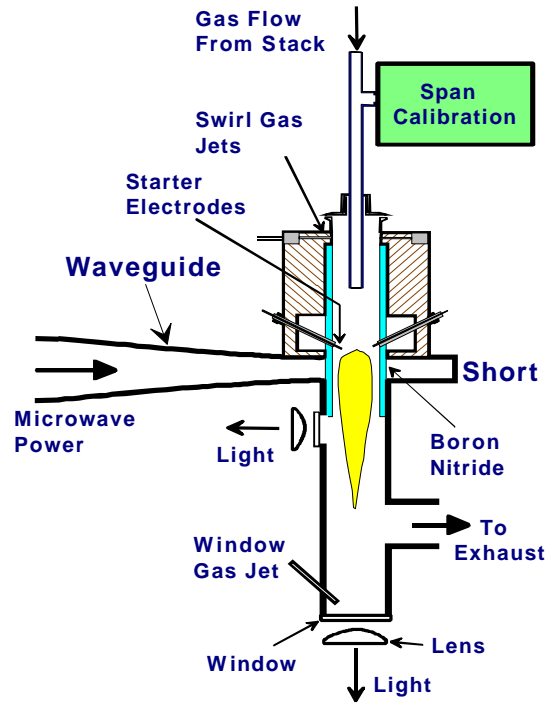


Figure 2. Microwave plasma details

leakage but, once properly adjusted, the microwave leakage meets OSHA regulations for kitchen ovens.

TABLE I Specifications of major MP-CEM components.

Component	Description
Microwave generator	1.5 kW nominal, 2.45 GHz ASTeX Model S-1500I or AX2050
Microwave chamber	Shorted WR284 brass guide; 38.1 x 76.2 mm or tapered 19.1 x 76.2 mm
Discharge tube	Boron nitride, 25.4 mm i.d., 3.18 mm wall or fused quartz, 28.6 mm i.d., 1.59 mm wall
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 lpm, N ₂ with 1 ml/min, nominal, solution uptake
Collection optics	UV grade fused quartz lenses
Fiber Optics	UV grade fused quartz 1.0 and 0.8 mm dia., 1, 2, and 3m lengths
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 range with ~0.05 nm resolution; tunable 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

A boron nitride or quartz tube penetrates through the waveguide perpendicular to the direction of microwave propagation a quarter wavelength back from the short. This tube directs the gas flow through the waveguide at an optimum position for plasma breakdown. A swirl gas is added at the sample line input to keep the plasma centered and off the discharge tube walls. The gas sample flow can be adjusted from 0 to over 28 liters per minute (lpm) as long as there is a swirl gas flow. For the EPA stack test described below, the nominal stack sample flow was 14 lpm corresponding to a stack flow velocity of 8.2 m/s (27 ft/s). Another gas jet is used to keep the viewing window clean. The swirl and window gas can be different from the sample line, and both air and nitrogen have been used. The flexibility of the MP-CEM to be able to put the viewing optics very close to the plasma is an advantage for reducing the detection limits of some metals such as mercury and arsenic. For example, the radial view near the waveguide as shown in Figure 2 minimizes the propagation path length for plasma emission through absorbing species.

A number of different spectrometers have been used with the MP-CEM. Two that were used at the EPA stack test are listed in Table I. Details of these spectrometers and sample MP spectrums have been described previously [14,15]. Improvements are still needed in the present spectrometer systems to better optimize the performance of the MP-CEM for multiple metals monitoring. Chromium, lead, and cadmium can be monitored with relatively inexpensive StellarNet detector arrays, but mercury, beryllium, and arsenic, with shorter wavelength UV emission require a more costly detector array with improved UV performance.

CALIBRATION

The real-time span calibration method assumes that aerosol metal salts generated by nebulizing a standard weak acid metal solution are representative of the stack entrained metals that are both speciated and unspicated. This is a reasonable assumption because the microwave plasma temperature has been measured to be very hot (>5000 K) [9, 14], hot enough to excite all metal species. This approach for span calibration has been previously used for real-time calibration of an air ICP [16].

The components of the real-time span calibration are shown in Figure 3. A spray chamber with a Meinhard nebulizer is connected to the branch off the sample line between the stack and plasma. A Masterflex C/L peristaltic pump connected to the liquid input of the nebulizer delivers a weak nitric acid standard solution containing a known concentration of all the metals being monitored (200 µg/ml each for the EPA test). A MKS Instruments flow controller provides pressurized nitrogen gas flow to the nebulizer at a rate of 1 liter per minute. The liquid feed rate into the nebulizer was approximately 1 ml/min for the EPA test. Since the nebulizer efficiency is very low, most of the standard solution liquid is collected in a waste flask. The waste flask must be connected with air tight tubing because it is part of the stack vacuum.

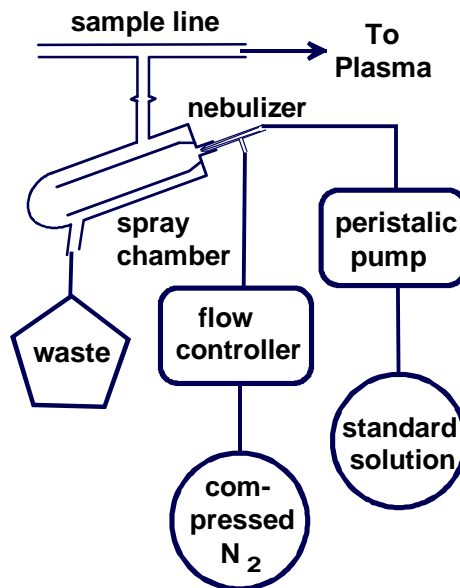


Figure 3. Span calibration system

The metals concentration injected into the sample line in µg/m³ is determined by the formula:

$$C_{span} = \epsilon \frac{XR}{F} \quad (1)$$

Where ϵ is the nebulizer, 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 m³/min. The solution concentration and pump rates are accurately known. The sample line flow rate is determined by calibrating an exhaust flow meter for sample line suction flow. The nebulizer efficiency is the least certain parameter that must be determined for this equation.

The unique accessibility of the present microwave plasma design, when not connected to the stack, allows for direct insertion, to the end of the sample line, of a dried microliter droplet of standard solution on a tungsten filament. Energizing the tungsten filament produces a pulse of metals signals for which the metal mass is known. Taking the ratio of this metal mass to that taken up by the nebulizer from the standard solution to produce the same integrated emission signal gives the metal mass transport efficiency of the nebulizer. Four Mienhard type A pneumatic nebulizers have been measured in this way to have efficiencies in the range of 0.5 – 1.0%. This result is in agreement with an alternative nebulizer efficiency measurement technique using sintered glass filters to collect the nebulizer aerosol.

It should also be possible in the future to establish the nebulizer efficiency by comparison to the EPA reference method when commissioning the installation of an MP-CEM. In this way the MP-CEM span calibration could be made directly traceable to the current regulatory standard.

EPA STACK TEST

The MP-CEM with its span calibration system was tested on the stack of the Rotary Kiln Incinerator Simulator at the EPA National Risk Management Research Laboratory in Research Triangle Park, North Carolina with seven other metals monitoring technologies [17]. Two EPA Method-29 sample collection reference methods were operated in parallel for relative accuracy determinations. The MP-CEM was the last monitor along the stack going away from the incinerator approximately 7 meters downstream from the nearest EPA reference method. 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 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 $\mu\text{g}/\text{actual m}^3$ and ten tests at a low concentration of 10 – 15 $\mu\text{g}/\text{actual m}^3$. Six hazardous metals (Hg, Pb, Cr, As, Cd, Be) were introduced into the secondary combustion chamber of the incinerator in a weak acid 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. The fly ash mainly contributed a background loading of interfering species such as iron.

The MP-CEM monitored three of the metals (Pb, Cr, and Be) simultaneously. The other three metals were not monitored at the time of the EPA test because the MP-CEM had not yet demonstrated sufficient sensitivity, nor did it have the additional spectrometer channels for Hg, Cd, and As detection. This additional capability is currently under development. Of the metals monitored, signals were acquired five times per second for Pb and Cr, and twice a second for Be. Each signal was corrected for background light in real-time and then displayed and recorded. An illustrative example of how the signals looked is shown in Figure 4, where the data for Pb is shown for the ninth high concentration test. The plotted data has been smoothed with a 6-second integration time constant.

A typical metals-spiked stack test started with the turn on of the aqueous metals feed to the incinerator. The MP-CEM metals signals would suddenly jump with the start of aqueous metals spiking as indicated by the “on” arrow in Figure 4. 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 plot in Figure 4 was set by this span signal, which corresponded to 92 $\mu\text{g}/\text{m}^3$ metals concentration in this case. The span signal could be turned on whenever and as often as needed to check the span calibration.

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. In Figure 4, the 6-second smoothing

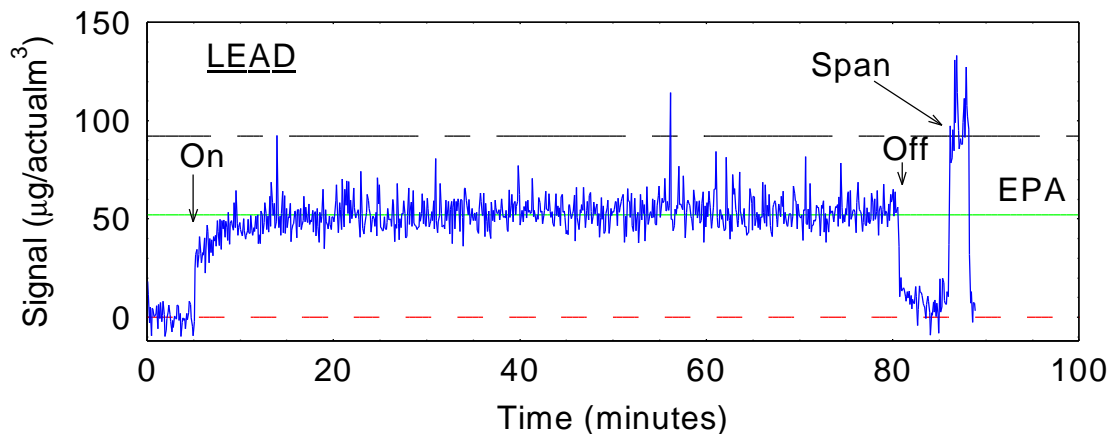


Figure 4. Lead signal for the ninth high concentration test with 6-second time resolution.

of the data has averaged out these transients. 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 real-time CEM signals were compared to the average of the two EPA reference measurements several weeks after the stack test, when the reference measurement analysis was completed. The single point EPA reference measurement for the test in Figure 4 is given by the straight line labeled EPA. In general there was good agreement between the average of the MP-CEM and the EPA reference measurements.

Table II lists the results for all the MP-CEM measurements, normalized to dry standard cubic meters. Most missing entries were caused by software deficiencies that were not fully debugged in time for this field test. The MP-CEM actually operated very reliably for all twenty tests. Table II contains a few more microwave plasma entries than the original report [17] because we did additional data recovery after the test. Also, some of the results differ because of to a correction for zero drift between the start of metals feed and the end of metals feed that was not taken into account at the time of the testing. This correction improved the agreement between the MP-CEM and EPA measurements for Pb and Be, but made the agreement worse for Cr.

TABLE II. Results for the MP-CEM and the EPA reference method in $\mu\text{g}/\text{dry standard m}^3$

Test #	Lead		Chromium		Beryllium	
	MP-CEM	EPA	MP-CEM	EPA	MP-CEM	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

Of the 44 individual test results 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 suspected that a cold probe in the stack between the microwave plasma and the EPA reference methods could have perturbed the metals concentration downward [18].

RELATIVE ACCURACY

The above data was analyzed for relative accuracy using EPA’s performance specification for CEMs [19]. According to this specification relative accuracy is defined by:

$$RA = \frac{|\bar{d}| + \frac{t_{0.975}}{\sqrt{n}}(SD)}{\bar{R}_{RM}} \quad (2)$$

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 as given in Table III. The results of evaluating the MP-CEM data with Equation (2) 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%. A small decrease in the span calibration would also improve the relative accuracies of lead and beryllium.

These results suggest that the EPA goal of 20% relative accuracy to the current reference method can be achieved by using a real-time span calibration. Further testing will be needed to confirm if the aerosol salts used for the span calibration are representative of the MP-CEM response to all stack entrained metal forms and species. If it is found that the aerosol salts do not accurately represent all stack exhaust situations, then it may be possible to use the EPA reference method to establish a site-specific calibration.

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

TABLE IV. Relative Accuracies

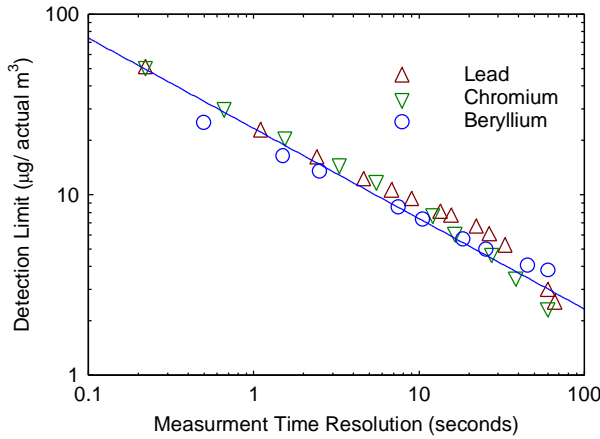
Metal	High Concentration	Low Concentration
Lead	20.5%	30.1%
Chromium	42.8%	42.5%
Beryllium	-	16.4%

DETECTION LIMITS

The detection limit is defined as a metal concentration that yields a signal which is equal to three times the standard deviation of the signal noise fluctuations. The standard deviation is a measure of how precisely a root mean square (rms) value can be assigned to a data set. There is generally an inverse relationship between the standard deviation and the signal integration time. The longer the time response of the measurement, the lower will be the detection limit. If the statistics of the plasma emission fluctuations is thermal or white noise, then the standard deviation will vary as the inverse square root of the signal integration time. In practice, the observed signal fluctuations are much greater than the classical thermal noise limit for incoherent light emission. They are also much higher than the detector background

electronic fluctuations. Apparently, for the present case, turbulent plasma flow may be the cause of the observed limiting signal fluctuations.

Analysis of the EPA stack test data shows that the standard deviation does indeed vary inversely as the square root of signal integration time as expected for white noise. This analysis is shown in Figure 5. Representative data sets of each of the three metals monitored were smoothed with a number of different smoothing times from 0.2 seconds (raw data) to 1 minute. For each smoothing time, a standard deviation was calculated and three times its value was plotted in Figure 5. 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 of the present analysis. For an integration time of 0.2 seconds the detection limit is approximately $50 \mu\text{g}/\text{m}^3$. At one minute it decreases to approximately $3 \mu\text{g}/\text{m}^3$, and it is projected to be $1 \mu\text{g}/\text{m}^3$ for an integration (measurement) time of approximately 10 minutes.

The current detection limit status of the MP-CEM for the six EPA stack test metals is summarized in Table V for one-minute response time. These values should be divided by a factor of the square root of two if comparing to other CEMs with a two-minute response time. The results for Pb, Cr, and Be are those obtained in the EPA stack test in undiluted stack gas plasmas with a 6.5% fraction of water. The results for Hg, Cd, and As were obtained in laboratory air plasmas with just a trace of water ($\sim 0.1\%$) from the aerosol injection. The side optics were used for mercury to minimize emission propagation path length through unexcited mercury vapor. There was a factor of three improvement in mercury detection by using the radial view versus the axial view.

The detection limits for cadmium and mercury are currently limited by reduced excitation efficiency in an air plasma and self-absorption. The detection limit for these metals is much lower in pure nitrogen plasmas, but the addition of a small amount of oxygen degrades performance by decreasing the excitation temperature [13]. In the case of arsenic, absorption of the short wavelength UV emission, by oxygen and related species, is the main cause of the high detection limit. Studies are continuing to better understand the performance of mercury, cadmium, and arsenic in air plasmas. Additional improvements are expected, particularly for arsenic, which has not yet been worked with extensively.

Table V. MP-CEM 60-second detection limits

Metal	Transition (nm)	Detection Limit (actual $\mu\text{g}/\text{m}^3$)
Pb	405.78	1.2
Cr	359.35	2.4
Be	234.86	3.6
Cd	326.12	10.5
Hg	253.65	20.0
As	197.26	144

DISCUSSION

The above results demonstrate that the MP-CEM with its real-time span calibration is a promising technology for achieving the hazardous multimetals monitoring requirements under consideration by the EPA. It has demonstrated a capability for both accurate and sensitive measurements for Be, Cr, and Pb in its first quantitative field-test on an incinerator stack. Additional development should add a similar capability for Hg, Cd, As, and other metals.

The microwave plasma generation hardware can be stack-mounted and operated at the stack temperature to simply the sample line and to eliminate any water condensation effects. Temperatures were at about 200 °C for the EPA test, but in an earlier experiment, reliable operation was demonstrated at over 600 °C [9]. Unlike earlier low power MIP devices, no resonator structure is used to sustain the plasma. Microwave power is beamed directly into the plasma in a standard waveguide that can be fabricated from refractory materials. It would be possible to implement this CEM upstream of exhaust quench nozzles and scrubbers for process control as well as downstream for compliance monitoring. Such an implementation would have significant advantages for improving measurement sensitivity to exhausted metals. The thermal process could be controlled for metals off gas content before such emissions could become detectable downstream of the scrubbers.

The 2.45 GHz microwave components used in the MP-CEM are readily available, inexpensive, and have a proven track record for reliability. The efficient coupling of the microwave power to the plasma, approaching 100%, and confinement of the microwaves inside the waveguide make this technology as radiation-safe to operating personnel as the common kitchen microwave oven. The spectrometer system would be the more expensive part of an MP-CEM. However, if only Cr, Pb, and Cd need to be monitored this too could be relatively inexpensive. For metals such as Hg and As, with prominent transitions at wavelengths less than 300 nm, more costly UV grade detectors would be needed. The development of a cost-effective spectrometer with high spectral resolution and wide wavelength coverage for simultaneous metals monitoring would improve the attractiveness of all plasma AES CEMs.

As yet, the MP-CEM is a relatively undeveloped technology compared to other technologies. Microwave plasmas in the past have had a reputation for not being as robust as ICPs and other plasma generation methods. However, present experience suggests the opposite is now true. Microwave plasmas can be sustained more reliably with lower power over a wider range of gas compositions, water loading, and flow volumes than ICPs. This is apparently due to advances in higher power microwave sources with high voltage power supplies having very low voltage ripple and the elimination of the resonator for plasma generation. With additional maturity, the MP-CEM should become a leading candidate for meeting future CEM metal monitoring needs.

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