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Monitoring**

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# Stack Mountable Microwave Plasma for Sensitive Real Time Calibrated Metals and Particulate Monitoring

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## ABSTRACT

A compact microwave plasma device that can be attached to a stack for near *in situ* atomic emission spectroscopy, with a real-time span calibration injector for accuracy, is under development for continuous metals monitoring. It uses a commercially available 2.45 GHz, 1.5 kW microwave source to generate a plasma in an undiluted, isokinetic flowing slipstream. The plasma is efficiently ( $> 98\%$  microwave to plasma coupling) sustained in a shorted waveguide, which together with a short sample line ( $< 50$  cm) is maintained at high temperature ( $> 150$  °C) to avoid condensation. Relative to other plasma based CEMs the microwave plasma has a significant advantage to continuously operate reliably in large volumes ( $\sim 50$  cm<sup>3</sup>) of fast flowing ( $\geq 14$  l/minute, up to 40 ft/sec) air or undiluted stack exhaust. A pneumatic nebulizer attached to the sample line can momentarily, on command, inject a known trace concentration of metals to provide a real-time span calibration whenever needed. Novel grating spectrometers using low cost detectors have been used for simultaneous multiple metals monitoring with continuous rapid signal acquisition ( $\leq 0.20$  s) making possible the observation of discrete particles. Since the particles are observed as plasma induced sources of light, the usual limits on monitoring discrete submicron particles by conventional external light instruments are not encountered. Detection limits for Be, Cr, and Pb of  $< 3$   $\mu\text{g}/\text{m}^3$  have been shown for one minute signal averaging in plasmas with 6% water content. A one minute detection limit for Hg of  $\leq 1$   $\mu\text{g}/\text{m}^3$  has been recently achieved in ambient laboratory air plasmas using a dedicated spectrometer. Lower detection limits are possible with longer signal integration time. Past testing on an EPA research incinerator demonstrated the capability for monitoring metal concentrations with a relative accuracy of 20% to EPA method 29.

## INTRODUCTION

There is a continuing need for better and more affordable air emissions monitoring technologies for the U. S. Environmental Protection Agency (EPA) Toxic Release Inventory (TRI) of hazardous chemicals and fine particulates. Such technologies are needed for research to better understand the environmental and health threat from various emission sources, for control of operations that produce TRI emissions, and ultimately for compliance with regulations. At present there is no single emissions monitoring technology that can observe the entire TRI list of chemicals along with the particulate size distributions, which are important for understanding pollution processes and for determining respiratory deposition and dose. In this report we focus on a microwave

plasma technology that has the potential to accurately monitor only the TRI metals along with aerosol particle size distributions down to sizes that usually cannot be discretely observed in flowing gas by conventional particle monitors.

Atomic emission spectroscopy of a plasma generated in stack exhaust or in an isokinetically extracted sample is a leading approach for real-time metals emissions monitoring. Among the various methods being used to generate a plasma for this application the microwave plasma torch has shown considerable promise. In a maiden field test attached to an EPA research incinerator stack its potential for compliance monitoring was readily demonstrated by achieving desirable sensitivity ( $< 3 \mu\text{g}/\text{m}^3$ ) and accuracy ( $\sim 20\%$ ) goals for a limited subset of the TRI metals for which it was instrumented (Be, Cr, and Pb)<sup>1,2</sup>. In earlier tests the microwave plasma device was fabricated from refractory materials and its potential as a control monitor was demonstrated by operating continuously **inside** a stack upstream of the scrubbers at temperatures  $> 650 \text{ }^\circ\text{C}$  and dense particle loading<sup>3</sup>. Recent laboratory development has focused on understanding the plasma mechanisms that limit *in situ* plasma detection sensitivity on some metals such as mercury<sup>4,5</sup>.

Characterization of particle size distributions along with discrete particle chemical composition has been accomplished in the past for aerosol particulate research with laser instruments. Multiple laser beams have been used to first measure size with low power scattering and then determine chemistry with a high power pulse to volatilize the particle for either atomic emission spectroscopy<sup>6</sup> or analysis in a mass spectrometer<sup>7</sup>. However, when the particle size is less than the wavelength of light, in the Rayleigh range, the scattered light scales as  $\sim r^6/I^4$  and individual small particles become difficult to observe.

More recently Hahn<sup>8</sup> has shown that a separate laser to illuminate a particle for size measurements is not necessary. The light emission from the high power laser spark that volatilizes the particle can be calibrated to determine size, assuming that only one particle is present per pulse. Furthermore, since an external source of light is not needed, the measured light signal is not constrained by the Rayleigh limit and smaller submicron particles can be studied. In another work Takahara et al<sup>9</sup>, have shown that light pulses due to particle transit into a continuous microwave plasma sustained in a resonator, in helium gas can also be calibrated to determine size. The light signal scaled as the particle size cubed, as expected for a signal dependent on the volatilized volume of a particle.

In this report we will show that total metals concentration and particle size distributions can be combined into one compact, stack mountable instrument using a continuous microwave plasma torch operating in undiluted stack exhaust or air. First we briefly review the hardware details and the past field results for monitoring Cr, Be, and Pb total metals concentrations in an EPA test incinerator stack. Next, recent laboratory results are described for Cd, and Hg monitoring showing how low detection limits in air plasmas can be obtained. Finally, the potential for real-time particulate size distribution measurements is pointed out in the earlier field data and in the more recent laboratory signals taken with rapid time resolution.

## HARDWARE

The major hardware elements of the microwave plasma continuous emissions monitor (CEM) for metals are shown in Figure 1. This system has been described in detail previously<sup>1,2</sup> and just a brief review is given here. The heart of the system is a microwave generated plasma sustained by a 1.5 kW, 2.45 GHz magnetron source with circulator and three stub impedance tuner from ASTex, Inc. The plasma is sustained inside a 25 or 28 mm internal diameter quartz or boron nitride tube which penetrates a shorted WR-284 (72 x 34 mm) waveguide through the center of its wide walls approximately one quarter wavelength (53 mm) back from the short. A narrowed waveguide (72 x 17 mm) has also been used to allow easier start up and stable operation at lower power (< 900 W) in air. Unlike all previously described analytical microwave induced plasmas (MIPs)<sup>10,11</sup> there is no resonance cavity. The microwave power is beamed directly into the plasma flame without obstruction making for very efficient microwave to plasma coupling at high power. Without adjustment of the three stub tuner coupling efficiencies are > 90% and approach 100% with adjustments. The plasma flame tends to fill the quartz or boron nitride tube and extend both upstream and downstream from the waveguide for total axial lengths in the 100 to 200 mm range, depending on the gas flow settings.

The sample gas to be monitored is introduced into the plasma by a 6-mm internal diameter quartz tube about 10 cm upstream of the waveguide. At the point where this tube enters the larger diameter plasma chamber, small tangential gas jets along the inside wall introduce a swirl gas flow which keeps the plasma flame off the wall. The plasma can be sustained over a wide range of sample gas flow of 0 – 30 liters per minute (lpm) corresponding to sample line gas velocities of 0 - 16 m/s (0 – 58 ft/s). Nominal sample gas flow used for most metals monitoring was approximately 14 lpm (27 ft/s) with a swirl gas flow somewhat less at about 10 lpm. A suction pump on the plasma exhaust establishes an isokinetic draw of the sample gas when this system is mounted on a stack. Both, a mechanical pump with heat exchanger<sup>1</sup> and a Penberthy jet pump<sup>3</sup> without moving parts have been used for this application. The exhaust is returned to the stack downstream of the sample collection line. For most laboratory measurements the sample and swirl gases come from pressurized sources and the suction pump is not used.

A unique feature of the microwave plasma CEM is a branch in the sample line with an attached span calibration system. An aerosol containing a known trace of metals can be momentarily turned on to flow into the sample line whenever needed to check monitor response. A Meinhard pneumatic nebulizer connected to a spray chamber, which filters out the large droplets, generates the aerosol. The nebulizer is operated with a controlled 1 lpm nitrogen gas flow which causes an uptake of approximately 1 milliliter per minute of standard solution containing the metals for which the CEM is to be calibrated. The metals transport efficiency from the standard solution to the sample line is calibrated off line by collecting filter samples and generally falls in the 0.3 – 0.9% range for this type nebulizer.

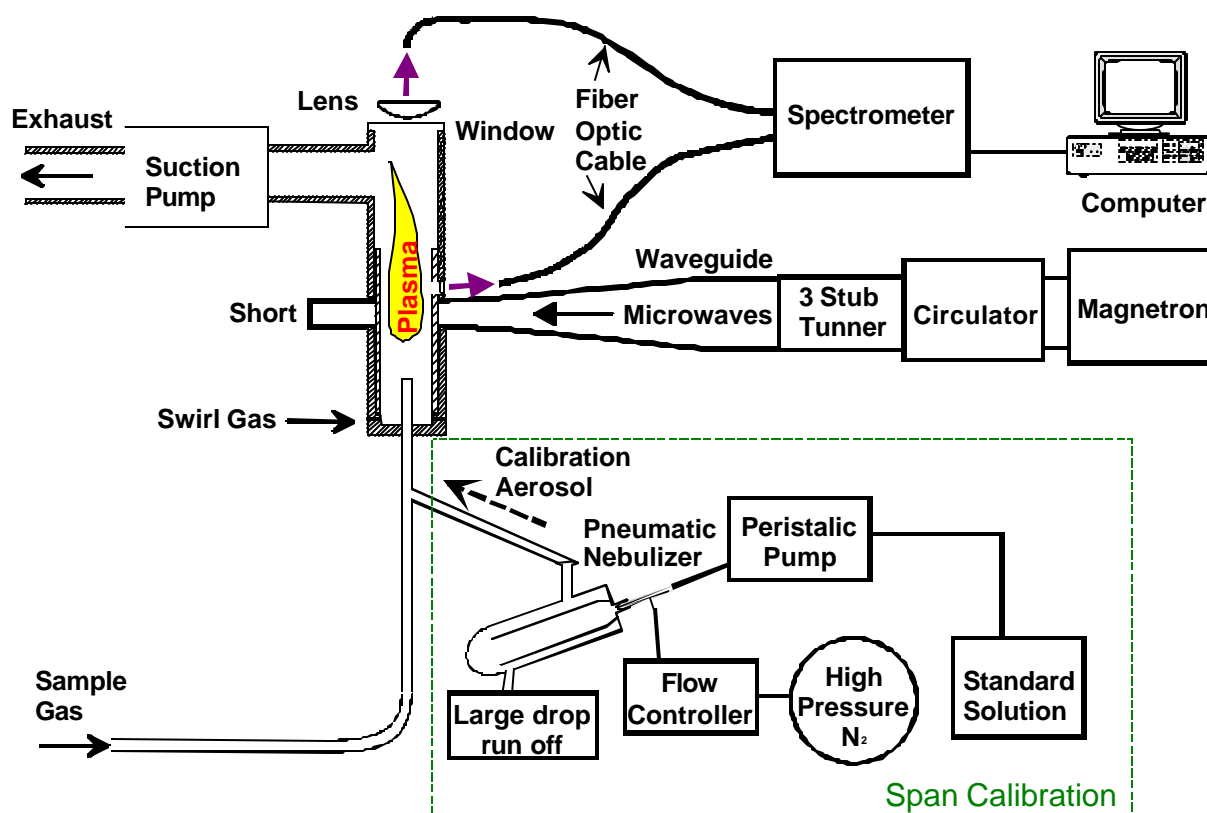


Figure 1. Block diagram of main components of the real-time calibrated microwave plasma CEM for metals.

The plasma emission light is viewed either axially from the entire plasma column or radially just upstream of the waveguide through fused quartz windows and lenses. Large core (0.8 – 1.0 mm), UV grade fiber optic cables of 1 to 3 meter lengths transport the light to spectrometers for analysis of the metals concentrations. A number of different commercial and custom fabricated grating spectrometers have been used to simultaneously monitor different metals<sup>1, 2, 12</sup>. In most cases, linear charged-coupled detector (ccd) and silicon diode detector arrays are used to monitor the strong metal emission transitions along with the plasma background spectrum around these transitions. Spectral data is acquired rapidly, several times a second, and processed in real-time for background emission<sup>2</sup>. A computer is used to display and store the resulting metal concentrations.

## PAST STACK RESULTS

In September 1997 the microwave plasma CEM was implemented on a stack at the rotary kiln incinerator simulator facility at the EPA National Risk Management Laboratory in Research Triangle Park for a two-week shake down and testing period. These results have been described previously<sup>1, 2, 13</sup> and are briefly reviewed here to demonstrate the stack mounted capability for sensitive and accurate metal concentration measurements. The results also demonstrate the unique capability of this CEM for **true continuous** (100% on line duty factor) rapid sub-second data acquisition. In addition, the robustness of the microwave plasma flame was show by operating reliably with good metals sensitivity on an undiluted slipstream that was 6% water vapor.

At the time of the stack implementation the microwave plasma CEM was ready only to monitor three of the fourteen TRI metals. These were beryllium, chromium, and lead. A total of twenty stack exhaust tests were carried out with fly ash and aerosolized solution containing the test metals introduced into the exhaust. Ten tests were at high concentration of 40-60  $\mu\text{g}/\text{m}^3$  (actual) and ten tests were at low concentration of 10-15  $\mu\text{g}/\text{m}^3$  (actual). Two Method-29 (collection of stack samples in filters followed by laboratory analysis) reference measurements located on the stack upstream from the microwave plasma CEM were made for each test and averaged for relative accuracy calculations.

The microwave plasma light emission was monitored axially for all the tests. The lead emissions data for the third low concentration test is shown in Figure 2. It is typical of the data for the other metals and tests. The lower plot shows the raw data as it was acquired at 5 times per second. At this time resolution the low background lead concentration due to the stack injection of the aerosol solution can not be resolved because of the statistical signal fluctuations. The prominent features are the discrete fly ash transients due to lead containing particles as they pass through the system and the span calibration bumps, at a concentration of 92  $\mu\text{g}/\text{m}^3$ , which were intentionally turned on at the two times indicated. This plot has a much higher y-axis concentration scale than the other two plots.

The middle plot of Figure 2 shows the same data after it has been smoothed to a 6-second time resolution. The steady background lead concentration at 11.5  $\mu\text{g}/\text{m}^3$  is now evident as well as the times when the aerosol metals stack spiking was interrupted and turned off. The fly ash spiking was not turned off between tests. At this time resolution the fly ash transients are mostly averaged out and do not contribute significantly to the total lead emission. Further smoothing of the data to one minute time resolution is shown in the top plot. The detection limit, defined as three times the standard deviation of the statistical signal fluctuations, improves inversely as the square root of time resolution from approximately 50  $\mu\text{g}/\text{m}^3$  in the lower plot to about 3  $\mu\text{g}/\text{m}^3$  in the upper plot. It is possible to continue smoothing the data to longer time resolutions to obtain even lower detection limits, but at some point 1/F noise will bound the ultimate achievable detection limit. This boundary has not been determined for the present system. Going out to two minutes smoothing to reduce the detection limit another factor of  $\sqrt{2}$  is possible.

The top plot of Figure 2 also shows the accuracy relative to Method-29. The reference methods produced only one point over the time period of each test, which is plotted as a dashed horizontal line superimposed on the microwave plasma data. In this particular test there was exact agreement between the microwave plasma CEM and the reference methods. Not all the tests were as in good agreement, but quite a few were. A relative accuracy (RA) evaluation of all the tests resulted with RA values of about 20% for lead and beryllium and about 40% for chromium<sup>1, 2</sup>. The error was systematic to lower values for the microwave plasma CEM and could be an artifact of a cold finger in the stack between the microwave plasma and the upstream location of the reference methods<sup>2</sup>.

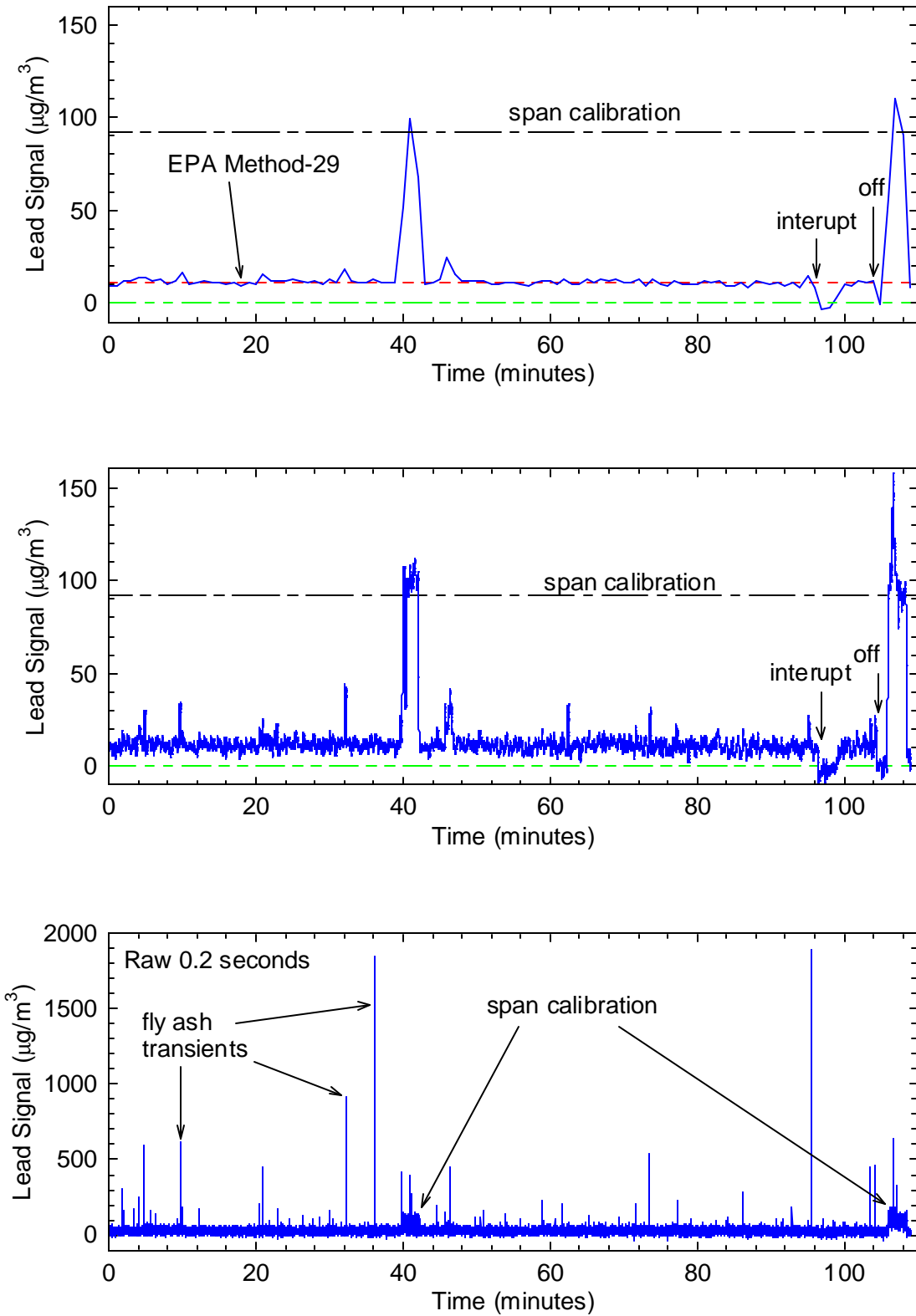


Figure 2. Stack test result for lead for the third low concentration run.

## RECENT LABORATORY RESULTS

Continued laboratory development of the microwave plasma CEM has focused on lowering the detection limits for cadmium and mercury. Plasma operation in a gas matrix of air or undiluted stack exhaust is not an optimum one for the detection of some metal atomic emission transitions. This is particularly true for atomic transitions that have a high excitation energy and those that terminate on the ground state. The electronic excitation temperature tends to be lower in molecular gas plasma, especially if oxygen is present. Studies of the microwave plasma have shown a dramatic increase in the detection limit of mercury on its usually strong 253.65 nm (excitation energy 4.89 eV) transition with just a small addition of oxygen (< 0.1%) to a nitrogen plasma<sup>4</sup>. The same is true for the usually strong 228.80 nm (excitation energy 5.42 eV) transition of cadmium. The observed reduction in emission for mercury was not due to the creation of a new UV absorption species in the plasma such as ozone<sup>4</sup>.

The likely effect of adding a molecular species such as oxygen to the plasma is to reduce the population of energetic electrons that excite the high energy levels. Reduced excitation not only reduces the number of emitting atoms but also increases the number of unexcited atoms that can reabsorb the emission. Therefore, a slight decrease in excitation of an allowed atomic transition that terminates on its ground state causes a much greater decrease in its emission due to the concurrent effect of self-absorption. Self-absorption was observed in an air microwave plasma and is shown in Figure 3 for the 228.80 nm cadmium emission. The lower plot in Figure 3 is for an axial view that is 10 cm longer than for the upper plot. With the longer light propagation path length through the plasma flame self-absorption becomes so strong that the 228.80 nm emission becomes an absorption feature. The adjacent 226.50 nm transition remains an emission feature because it is due to an ionized state and therefore is not absorbed by unexcited cadmium.

The strategies for improving the detection limit of metals that are adversely effected by a molecular species in the plasma are: 1) use an atomic emission transition that is not a strong absorber in its ground state or, 2) make the light propagation path as short as possible through unexcited regions of the plasma. The first strategy was effectively used for cadmium because cadmium has a number other prominent transitions that can be used for detection. Though the 226.50 nm transition shown in Figure 3 was a candidate, a better one in the present microwave plasma proved to be the 326.1 nm (excitation energy 3.80 eV) transition. A detection limit of 8  $\mu\text{g}/\text{m}^3$  was achieved for one-minute time resolution in air at 14 lpm sample flow with an unoptimized spectrometer<sup>5</sup>.

In the case of mercury the second strategy had to be used because there were no alternatives to the 253.65 nm transition in the present microwave plasma. The light propagation path length was made shorter by more than a factor of ten by viewing the emission from the side as shown by the side fiber optic in Figure 1. The view was put as close as possible to the microwave waveguide driven region of the plasma where the electron energies would be expected to be highest. Furthermore, the swirl gas was



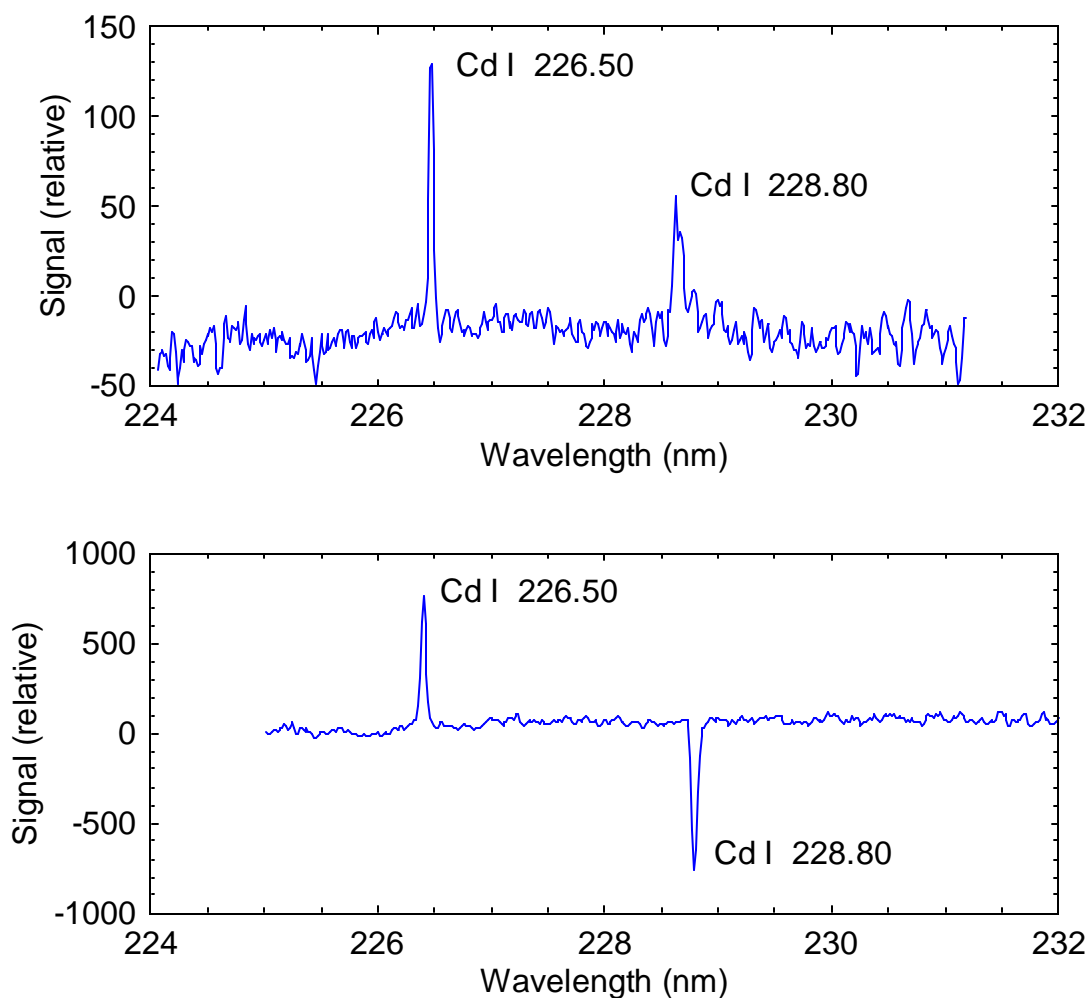


Figure 3. Cadmium spectra showing emission and self-absorption. Bottom spectrum is for a longer light propagation path length through the plasma.

changed to nitrogen rather than air which increased the mercury signals by removing the effects of oxygen in the plasma edges through which the light emission was viewed.

With the optimized side viewing geometry and an optimized spectrometer a study of the mercury detection limits versus gas flow was carried out at a microwave power of 1.5 kW. The results are shown in Figure 4. Mercury detection limits for one-minute time resolution are shown versus the sum of the sample and swirl gas flows. The sample flow volume varied from a minimum of 5 lpm to a maximum of 14 lpm in this data set with the swirl volume less than or about equal to the sample flow. The lower trace is for an aerosolized mercury salt from a weak HNO<sub>3</sub> acid solution injected into a nitrogen sample gas flow. The upper plot is for the same salt in an air sample gas. The swirl in both cases is nitrogen. At the lower sample flow the detection limits are about 0.2 and 1.0  $\mu\text{g}/\text{m}^3$  for the nitrogen and air plasmas, respectively, and increase to about 0.5 and 1.7  $\mu\text{g}/\text{m}^3$  at 14 lpm and low swirl flow. This is better sensitivity than current commercially available mercury CEMs that can only detect mercury<sup>13</sup>.

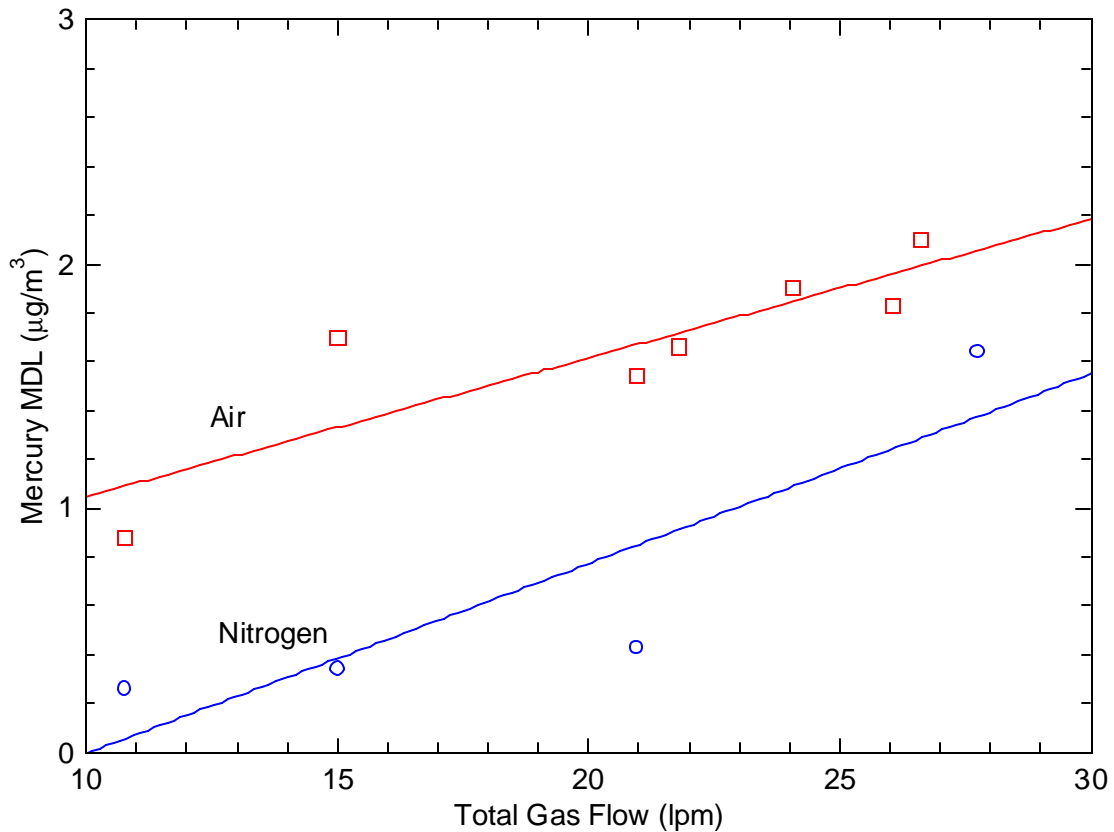


Figure 4. Mercury detection limits in air and nitrogen plasmas as a function of the sum of sample and swirl gas flow.

## POTENTIAL FOR PARTICULATE MEASUREMENTS

The mode of operation of the stack mounted microwave plasma described here provides the capability to monitor particle numbers and size distributions. As shown in the discussion of past stack results the microwave plasma operates in true continuous mode (100% duty factor) with rapid sub-second signal acquisition. Consequently it resolves and detects every particle entrained in the gas flow passing through the plasma.

The prominent lead containing particles are evident in the bottom graph of Figure 2. At the same time the iron signal at 360.88 nm recorded is shown in Figure 5. The amount of iron present in the fly ash of this stack test was many thousands of times larger than the hazardous metals. If the lower trace in Figure 2 is plotted on the same light emission scale in Figure 5, the highest lead transients would be lost within the first two tick marks of the iron graph. As expected there are many more, and larger, iron particles than those with lead. The mean size of the fly ash particles was 6 µm. This data demonstrates that, with some additional work, the stack mounted microwave plasma can be adapted to monitor and characterize particle distributions.

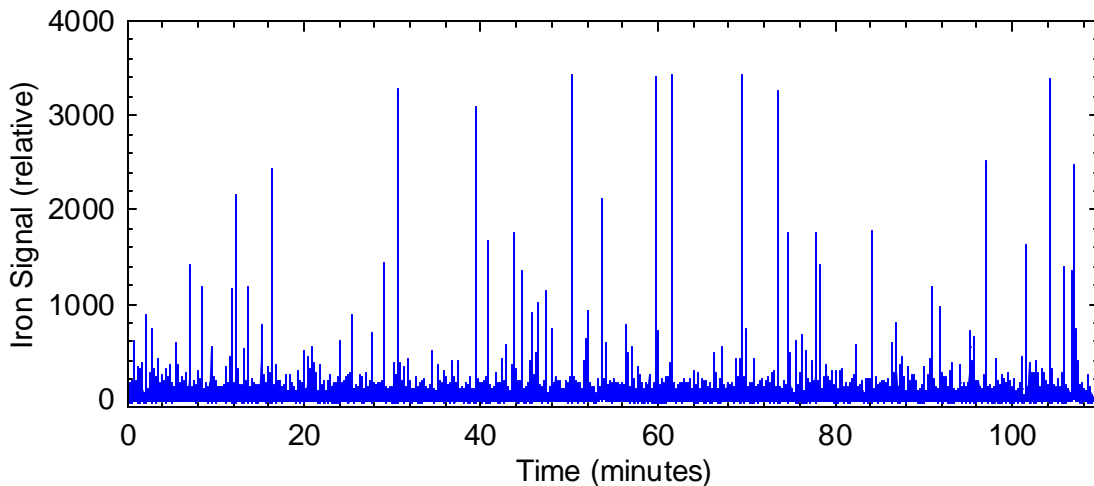


Figure 5. Iron emission data taken at the same time as the lead data in Figure 2.

However, there is a unique feature to this capability. The individual particles become visible by a mechanism that is significantly different from conventional particle monitors. There is no external light source. The particles are induced by the plasma to emit light. Consequently the discrete particle size that can be observed is not constrained by Mie or Raleigh scattering theory. Much smaller particle sizes can be monitored along with the larger ones. It should be possible to discretely monitor all particle sizes down to fine ( $< 2.5 \mu\text{m}$ ) and ultrafine ( $< 0.1 \mu\text{m}$ ) sizes for which commercially available monitors are not currently available.

Evidence for observing sub-micron particles is given in Figure 6. Axially viewed Microwave plasma emission light is shown at a wavelength of 326.106 nm corresponding to the wavelength of the strong cadmium transition. The span nebulizer was used to introduce an aerosol into the plasma and the signal was acquired at approximately 7 times a second. A heater tape around the sample line raised the temperature above  $100^\circ\text{C}$  to prevent liquid droplets from entering the plasma. It has been shown that the particle salts generated by a nebulizer in this way are much smaller than  $1 \mu\text{m}$ <sup>8</sup>. In the first half of the trace in Figure 6 a blank solution is used and then, where indicated by the arrow, replaced by a solution containing a weak  $\text{HNO}_3$  acid solution with cadmium. The inherent fine to ultrafine particulate nature of the cadmium introduced into the plasma is evident by the significant increase in the signal fluctuations when the metal salt is present. This behavior is typical for other metal aerosols too.

The axial optics for the data in Figure 6, and also for the data in Figures 2 and 5, viewed most of the plasma volume ( $\sim 50 \text{ cm}^3$ ) and therefore particle overlap is significant. A different viewing optics arrangement to view a much smaller volume would be able to observe discrete fine and ultrafine particles. Diffraction limited viewed volume fractions less than a cubic millimeter are possible. With optimized viewing geometries the microwave plasma would make possible monitoring discrete particles over a dynamic range of sizes much greater than currently possible.

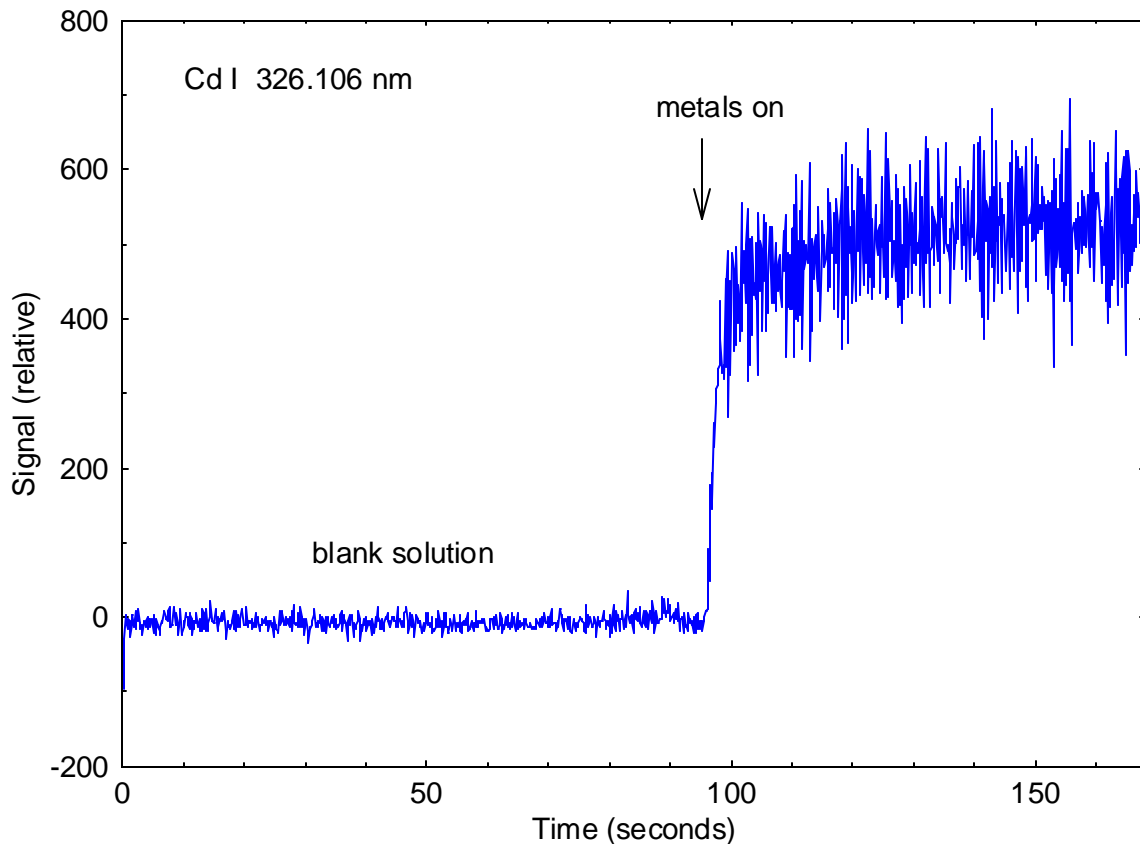


Figure 6. Evidence of sub-micron particle resolution when aerosolized metal salts are present in the plasma.

## CONCLUSIONS

The compact, stack mountable microwave instrumentation described here with its attached span calibration system and fast signal acquisition represents a significant advance in stack emissions monitoring capability. The results to date show that 2.45 GHz microwave power ( $\leq 1.5$  kW) in a simple shorted waveguide can sustain a reliable, continuous (100% on line duty factor), large volume ( $\sim 50$  cm<sup>3</sup>) plasma in a stack slipstream (or inside the stack<sup>3</sup>) for atomic emission spectroscopy of stack emissions. Good measurement accuracy (RA  $\leq 20\%$ ) for metals concentration is readily achieved with the attached span calibration injector. By this method measurement accuracy can be maintained over variable exhaust gas-matrix conditions and other field variables such as optics cleanliness and electronic drifts. Tests at an EPA research incinerator with reference Method-29 have confirmed the capability for accurate measurements. In addition these test have shown low detection limits  $< 3$   $\mu\text{g}/\text{m}^3$  for Be, Cr, and Pb for one-minute time resolution in undiluted stack exhaust plasmas having a 6% content of water.

Recent laboratory development has overcome the difficulties with monitoring mercury in an *in situ* or near *in situ* plasma gas matrix by determining the plasma mechanisms that limit Hg 253.65 nm emission. These mechanisms were identified as reduced electronic excitation and self-absorption. As a result of this knowledge the collection optic views and spectrometer configuration have been reengineered to improve performance. A one-minute mercury detection limit in an air plasma of  $\leq 1 \mu\text{g}/\text{m}^3$  has been achieved in the laboratory. Though a stack test will be needed to confirm this performance in the field, even with some degradation this level of performance rivals the best capability of currently available commercial technologies that can detect only mercury in more complex instrumentation packages.

The microwave plasma monitoring capabilities described here go beyond metals concentration measurements. Because of the fast signal acquisition, particle size distributions and discrete particle elemental compositions can be observed. Much smaller particle sizes can be observed than has been previously possible because of the fundamentally different nature by which the particles are made visible. They are induced by the plasma to be sources of light rather than passively scattering, shadowing, or diffracting light from an external source. The usual limits on particle size resolution are thus avoided. For the first time a potential continuous capability to monitor fine and ultrafine particulate matter has been demonstrated without compromising the ability to observe larger particles. Human respiratory deposition/dose of hazardous chemicals depends in part on the particulate size distributions so such measurements are important to assess the full impact of emissions on human welfare.

As public concern and government regulations increase to control and monitor stack emissions of potentially polluting processes, there will be a growing need for real-time emissions monitoring technologies for numerous emissions parameters and chemicals. Monitoring technologies that can provide measurements of multiple parameters and chemicals would represent a significant cost savings and reduction in complexity of stack implementation. Such technologies would also be of value in researching sources of emissions to provide an understanding for improving processes for reducing emissions. The microwave-plasma monitoring technology described here, when fully developed, could make a significant contribution in that direction.

## **ACKNOWLEDGEMENTS**

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## KEY WORDS

Continuous emissions monitor, metals, particles, source monitoring, mercury, calibration