PFC/JA-96-10

Microwave Plasma Continuous Emissions Monitor for Trace Metals

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March 1996

Submitted to *Review of Scientific Instruments.*

Supported by Battelle - Pacific Northwest Laboratory as part of the Landfill Stabilization Focus Area, Office of Technology Development, Environmental Management, U. S. Department of Energy.

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Abstract

A microwave plasma continuous emissions monitor has been successfully demonstrated for sensitive (< 1 ppb), real time measurements of trace metals in furnace exhaust. The instrument uses a robust, up to 1.5 kW, 2.45 GHz microwave plasma sustained in a portion of the undiluted furnace exhaust flow for atomic emission spectroscopy. The waveguide device is constructed of refractory materials compatible with high temperature environments (>500 °C) and is flange mountable into the inside of the furnace exhaust duct. Fused quartz fiber optics in close proximity to the plasma flame transmit the UV through visible emission (190 - 690 nm) to three spectrometers for simultaneous monitoring of several metals. This instrument has been used for continuous monitoring for a 49 hour period with 0.5 second time resolution on a dc graphite electrode arc furnace during a soil vitrification test. Results are presented for chromium, manganese, and iron emissions during soil loading operations.

I. Introduction

Strict new laws for the prevention of hazardous metals air pollution are being implemented in the United States and the European Community. The U. S. Environmental Protection Agency (EPA) is writing new regulations for the control of twelve metals (Ag, As, Ba, Be, Cd, Cr, Hg, Ni, Pb, Sb, Se, Tl) that are known to be toxic or carcinogenic health risks to the human population. These new rules will require the use of continuous emissions monitors on furnaces and incinerators used in many thermal process in the manufacturing, waste remediation, and power production sectors. Such monitors would be of value not only for assuring compliance with the new regulations, but could also make the use of possible feedback control of these processes.

To date no commercial instrumentation is available for real time monitoring of trace metals in furnace exhaust. Compliance with emissions in the U. S. is currently achieved with EPA method 29 which requires collecting samples in filters and in an impinger solution sample train. The collected samples are then set to a laboratory to be analyzed by conventional methods such as atomic absorption spectroscopy after heated volatilization, atomic emission spectroscopy in a plasma, or x-ray fluoresence. It can take more than one day to get averaged results. Real time control is not possible with this method, nor does it provide insights into transient effects in the thermal process that can affect emissions.

The recognized need for continuous emissions monitors has stimulated work to adapt laboratory elemental analysis instruments for use in the field, as well as the development of more novel instrumentation. The most promising instruments use a plasma for atomic emission spectroscopy [1] and only differ in the method used to create the plasma state in a portion of the exhaust gas. Plasmas are ideally suited for total metals emission measurements because they are sufficiently hot to atomize and excite all elements present in the exhaust in whatever molecular form (speciated or unspeciated) or state (particulate, droplet, or vapor) that they may be in. The plasma can therefore accept all exhaust entrained forms of metals like EPA method 29, but with the capability for real time analysis via atomic emission spectroscopy.

Much work has been done to adapt a common laboratory tool, the inductively coupled plasma (ICP), for real time measurements [2-5]. A difficulty with this approach is that the stability of an ICP is very sensitive to gas composition and flow rate which are normally precisely controlled in the laboratory. A specially designed sampling interface much more complicated than used in EPA method 29 is generally required to provide an acceptable flow to the ICP in order to make possible isokinetic sampling of the exhaust in real time. It has been noted that this sampling interface can be a source of error [3].

Laser spark based instruments have also been tested [6,7]. The focusing of a high power pulsed laser beam into the exhaust gas allows true *in situ* measurements.

However, the instantaneous volume sampled has a cross-section of only a few tens of micrometers due to the small focused spot size, and the sample time is only a few tens of nanoseconds per second due to the short laser pulses (~ 8 ns) and low pulse repetition rate (few Hz). Combining these factors it can be shown that laser spark methods monitor a plasma volume per unit of time that is many orders of magnitude smaller than EPA method 29. Consequently this method is less sensitive to trace metals, particularly if they are in the vapor state.

In this report we present a novel new approach using a microwave plasma which overcomes the disadvantages of both the ICP and laser spark based instruments. Microwave induced plasmas like ICPs are used in the laboratory for sensitive elemental analysis [8,9]. Their application to real time trace metals monitoring in furnace exhaust has been recently proposed [10] and a laboratory instrument has been adapted for real time monitoring of reactive gases used in semiconductor production [11]. Relative to ICPs, microwave plasmas are more robust and can directly accept a large undiluted exhaust flow. In addition, we show here that the microwave waveguide structure in which the plasma is sustained can be fabricated of refractory materials and placed inside the furnace exhaust stack. This makes possible *in situ* sampling and monitoring similar to the laser spark techniques, but with large sampling volumes comparable to EPA method 29 for high sensitivity measurements.

II. Experimental Apparatus

The major hardware elements of the microwave plasma continuous emissions monitor (CEM) are illustrated in the block diagram of Figure 1 and the parameters are given in Table 1. The microwave source was a 2.45 GHz magnetron with a maximum output power of 1.5 kW which was operated as low as 0.5 kW for many of the measurements present here. A waveguide circulator at the output of the magnetron directed reflected power into a dump and incorporated a reflected power detector. The waveguide transmission line included a triple stub tuner to match the impedance of the waveguide from the source to the plasma waveguide section to minimize reflected power. The reflected power could typically be adjusted to less than 2% of the forward power. The rectangular waveguide in this system had internal dimensions of 72.1 x 34.0 mm (WR284 band).

The plasma itself was induced in a shorted length of waveguide one quarter wavelength back from the short. This waveguide was either full size WR284 or tapered to half width (72.1 x 17.0 mm) in the various plasma device configurations tested. Figure 2 illustrates a cross sectional view of a configuration used on the Mark II furnace. The shorted waveguide was fabricated from fine grained graphite with 12.7 mm thick walls into which was inserted a truncated brass waveguide from the triple stub tuner. A 28.6 mm internal diameter (i. d.) boron nitride (BN) tube with a 3.2 mm thick wall formed a gas flow channel through the waveguide along the direction of the electric field (through the wider walls). The plasma was sustained in the center of this BN tube.

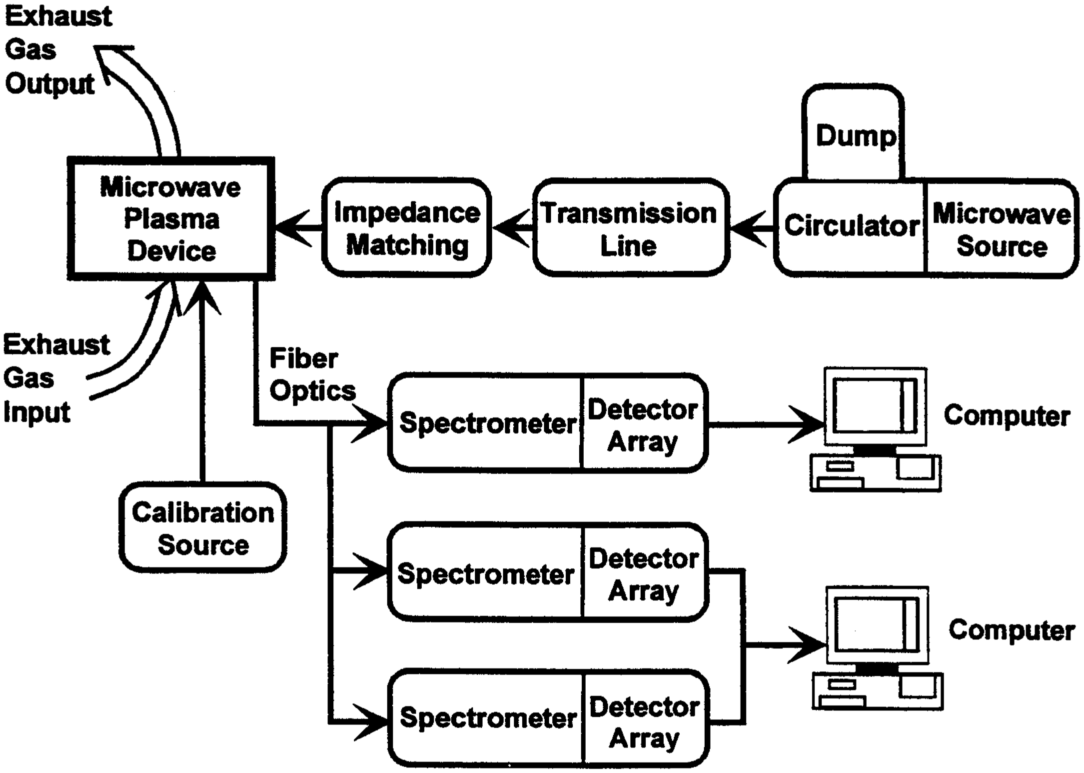

Figure 1. Block diagram of the major components of a microwave plasma continuous emissions monitor.

An alumina tube with a 4.8 mm i. d. and 2.4 mm walls was located with its end between 0 and 5 mm back from the inside waveguide wall surface and centered in the flow channel on the gas input side of the waveguide. It was found that for longitudinal gas flow without any rotation, the thermal emission from the end of this alumina tube was necessary to keep the plasma centered in the flow channel. This tube was also used for inserting calibration samples and a Hemholtz antenna for spark starting the plasma.

The furnace exhaust gas was intercepted and directed into the plasma by a 28.6 mm i. d., 1.6 mm wall stainless steel pipe which was bent into a position to sample the exhaust flow in the center of the exhaust duct. The total length of this input pipe was 48 cm for the furnace measurements presented here. A Penberthy jet pump was used as a suction pump to maintain an adequate flow through the waveguide and returned the gas to the furnace exhaust duct after passage through the plasma. The nominal gas flow through the waveguide was in the range of 10 - 30 L/min. It would be possible to establish isokinetic sampling by proper adjustment of the suction pump, but this was not attempted for the present measurements.

The plasma light was transmitted to the spectrometers by fused quartz fiber guides having a high temperature gold cladding usable up to 750 °C. There was one

Table 1. Apparatus and Operating Conditions

Component	Description
Microwave generator	1.5 kW, 2.45 GHz magnetron source, ASTeX Model S-1500i
Microwave chamber	shorted graphite waveguide, WR284
Discharge tube	boron nitride, 28.6 mm i.d.
Gas flow	10 - 30 l/min. at atmospheric pressure
Calibration	direct insertion of dry samples
Fiber optics	fused quartz 400 μm core with gold coating, Fiberguide Industries SFS 400/440G
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	Instruments SA Model THR-640, 0.64 m Czerny Turner spectrometer with 2400 groove/mm grating, ~ 10 μm adjustable slit, Princeton Instruments Model 1RY-512W intensified 512 element detector array, ~ 6.5 nm instantaneous spectral range with ~ 0.01 nm resolution tunable over 183 - 600 nm

400 μm core diameter fiber for each spectrometer. The fibers were brought to the plasma flame through a 1.6 mm i. d. alumina tube embedded in the graphite waveguide wall as shown in Figure 2. They penetrated the BN liner and viewed straight across the plasma about 11 mm down stream from the inside waveguide wall. Close proximity to the plasma tended to keep the fiber viewing ends clean.

For the furnace measurements the microwave plasma device assembly was enclosed in a gas tight stainless steel box and mounted to the side of the furnace exhaust duct. It was located immediately adjacent to the furnace to directly monitor the hot unflitered exhaust up stream of a water quench and scrubbers. Thermocouples were also located on the input pipe, graphite waveguide, and jet pump to monitor temperatures during operation.

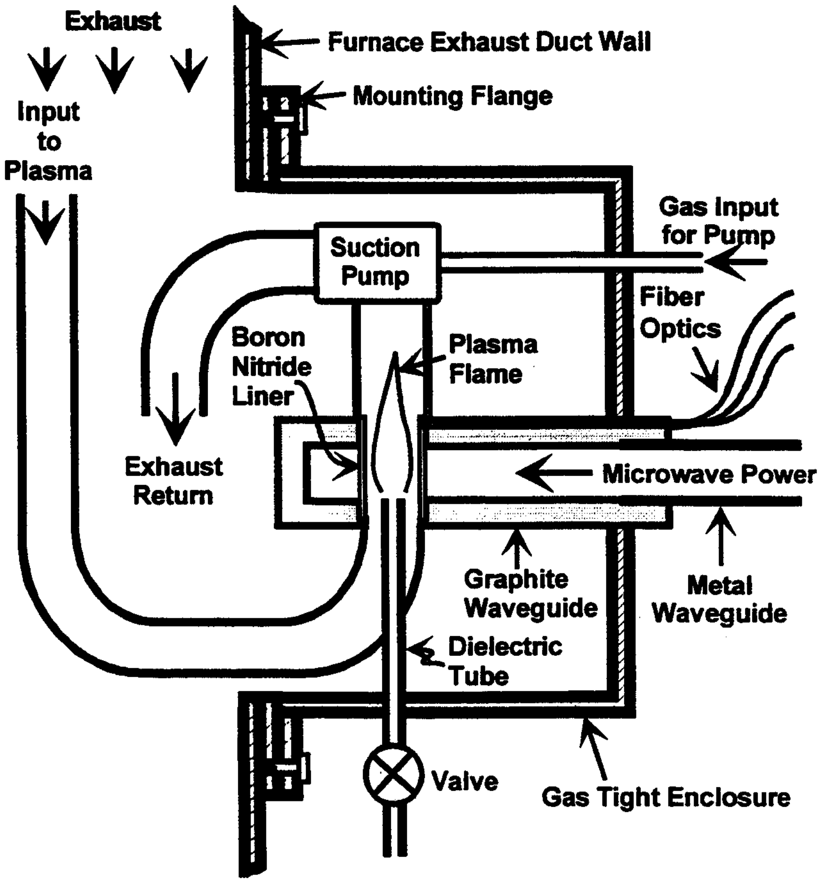

Figure 2. Cross-sectional view of the flange mountable microwave plasma device used for continuous emission monitoring on a furnace.

The plasma flame could be oriented in any convenient direction. In the first configuration tested, shown in Figure 2, the plasma flame was horizontal along the direction of the exhaust duct but directed back toward the furnace. This allowed easier access to the base of the plasma flame away from the furnace. In a second configuration, used for the furnace measurements presented here, the waveguide was rotated 90° to the plane of Figure 2 to orient the flame vertically downward. This allowed for any debris to fall through and not accumulate inside the waveguide, as well as for easy access to the base of the flame from the top. The suction pump was displaced and a trap for debris was provide in this orientation.

Three grating spectrometers were used for the plasma light emission measurements as described in Table 1. A pair of low resolution (~ 1.3 nm) spectrometers each with a 1024 element CCD array detector provided an instantaneous survey of the entire 190 - 690 nm spectral range. A high resolution spectrometer (~0.01 nm) with a 512 element intensified silicon diode detector array was used for quantitative measurements in a ~6.5 nm instantaneous spectral range which was tunable over 183 - 600 nm. Spectra could be acquired as rapidly as 7 and 17 ms, respectively, but were typically integrated for 0.5 second periods during the furnace measurements to conserve computer storage memory. Signals were displayed in real time by a pair of computers.

III. Laboratory Measurements

The performance of this instrument was first evaluated in the laboratory. For most of these tests the plasma flame was orientated vertically upward without a suction pump. Gas flow was blown in from compressed sources or with a fan for tests with laboratory air.

The robustness of the microwave plasma for direct undiluted sampling of furnace exhaust was first established by operation in a variety of gases and with particulate and droplet loadings. Stable plasma operation was achieved with N_2, air, and CO_2 gases, with 100 mesh (149 μm screen spacing) iron filings, furnace soot particulates, and with up to 1 mL/min of water injected into the gas flow with a Meinhard Nebulizer. The flow volume could also be increase as high as 75 L/min for microwave power over 1 kW. It was readily apparent that the microwave plasma would operate stably under whatever gas matrix and flow conditions that may be found in a furnace exhaust.

Next, the plasma gas temperature was determined spectroscopically. For these measurements and the following detection limit measurements nitrogen gas was used as the working medium because it was representative of the nitrogen purged furnace. Figure 3 shows the (0, 0) band of the first negative system of the N_2^+ ion from a composite of 5 adjacent spectra taken with the high resolution spectrometer. We were able to identify the R24 through R97 rotational transitions and to plot in Figure 4 $\ln(I/(N'+N''+1))$ versus $N'(N'+1)$, where I is the line intensity, N' is the upper level quantum number, and N'' is the lower level quantum number. The slope of such a plot for the odd and even lines separately is equal to $2.983/T$ where T is the molecular rotational temperature in degrees K [12, 13].

The 5700 ± 200 K temperatures determined in this way are considered to be representative of the gas temperature in the microwave plasma because of the rapid collisional relaxation time of rotational levels. These measured temperatures are sufficiently high to vaporize particulates and droplets, decompose molecular species, and excite atomic transitions of all elements that might be entrained in the gas flow through the plasma. The effectiveness of the plasma to monitor all metal elements in whatever form was corroborated by the observation of atomic uranium and zirconium when refractory oxide samples (melting temperatures 2300 and 2700 °C, respectively) of those elements were inserted into the plasma, as well as the observation of mercury in its vapor state [10].

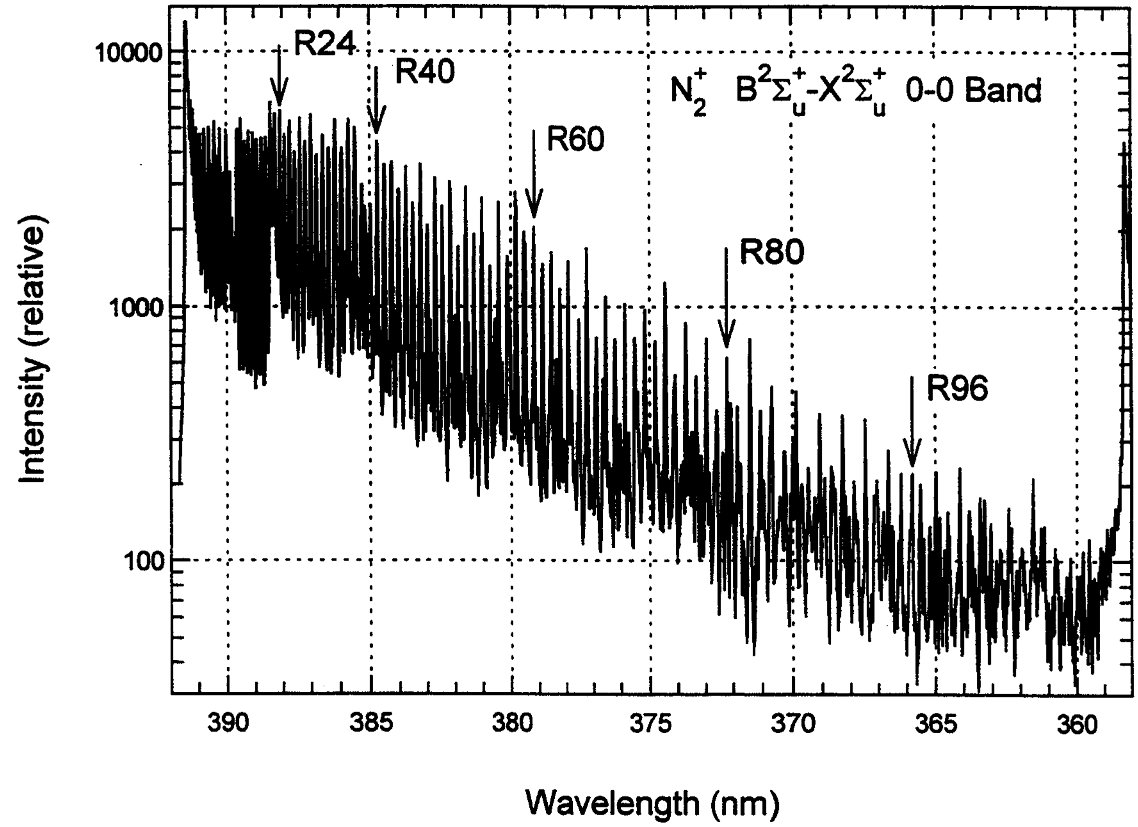

Figure 3. The rotational emission structure of the (0,0) band of the first negative system of the N_2^+ ion in the microwave plasma for 508 Watts forward power and 12 L/min nitrogen gas flow.

The sensitivity of the microwave plasma device was tested next by the determination of the threshold detection levels of 10 of the EPA metals. These measurements were accomplished by direct insertion of dry samples into the base of the plasma on the tip of an alumina rod. Two types of samples were used. SPEX Industries G Standards of graphite diluted powders containing 49 common elements, most in oxide forms, and dried droplets of Alfa ÆSAR multielement standard solutions containing 100 μg/mL of the metals of interest. The N_2^+ emission bands were quenched when these samples were inserted into the plasma, though CN bands were present under some conditions with the SPEX powders.

A few hundred nanograms of the metal to be tested was deposited on the tip of the alumina rod by weight or volume, respectively. Upon insertion into the plasma the spectral emission signal for a strong transition was integrated during the burn off time period. The threshold detection level was then determined by dividing the mass of the sample by the integrated signal level and multiplying by three times the standard deviation of the background noise level for an equivalent integration time. These detection limits are listed in Table 2 along with the spectral transition and the burn off

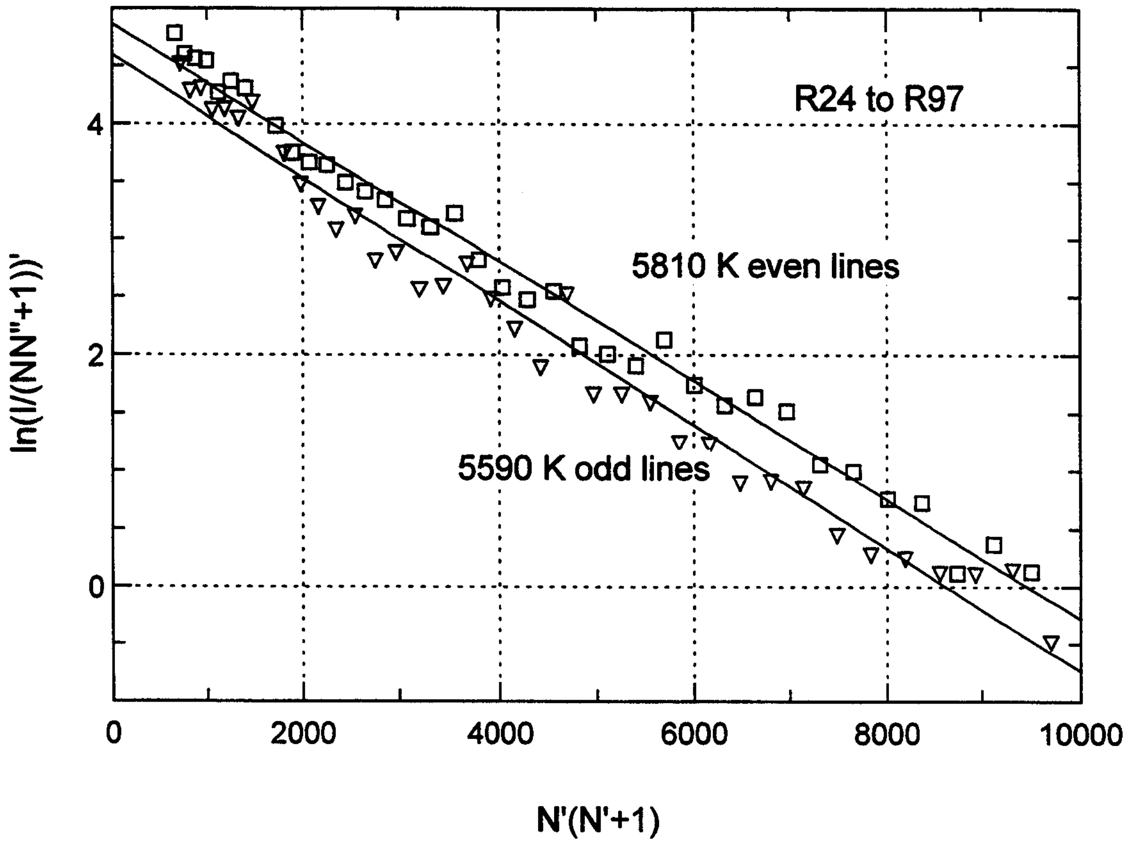

Figure 4. Determination of the rotational temperature of the N_2^+ ions from the spectrum of Figure 3.

signal integration time used to determine them. In a few cases the sample was not completely burned off in the time period monitored and in those cases the detection limit is shown as an upper limit.

The first detection limit column in Table 2 lists the absolute mass threshold in nanograms obtained as described above. The second column lists a concentration detection limit in µg/m^3 estimated by dividing the mass threshold by the total gas flow volume through the plasma during the signal integration time period. The finial column lists a concentration detection limit in parts per billion assuming the concentration in the second column is uniformly dispersed through a gas at standard pressure and temperature. These detection limits are generally not as low as the best laboratory microwave induced plasma results given in [8], but are comparable to ICP results for real time use [2-5] and much better than the laser spark techniques [6,7]. They clearly demonstrate that this microwave plasma instrument has the potential for high sensitivity trace metals measurements.

Table 2. Laboratory Detection Limits in Nitrogen

Metal	Transition (nm)	Burn Off* (sec)	Detection Limit (ng)	($\mu g/m^3$)	(ppb)**
Be	234.9	17	0.16	0.04	0.1
Cd	228.8	6.8	0.17	0.09	0.02
Ag	328.1	>11	<0.24	<0.08	<0.02
Ba	553.6	>32	<0.68	<0.08	<0.01
Sb	231.1	>30	<0.89	<0.11	<0.02
Pb	283.3	4.2	1.1	0.9	0.2
Ni	341.4	>36	<1.1	<0.12	<0.05
Cr	357.8	2.6	1.3	1.8	0.8
Hg	253.7	4.2	2.9	2.5	0.3
As	235.0	6.4	5.8	3	1

* Initial sample mass 200 ng except 800 ng for Pb and As

** At standard pressure and temperature

IV. Furnace Measurements

Real time trace metal emission measurements were carried out on Mark II, a pilot scale DC graphite electrode arc furnace at the MIT Plasma Fusion Center [14]. This furnace has been developed for the virtification of mixed buried wastes in the DOE complex. It has the capacity to process up to 300 kg of soil per hour with up to 1 MW of electrical power. For the test with the microwave plasma CEM the furnace was filled initially with approximately 200 kg of clean soil from the DOE site near Idaho Falls, with another 200 kg of soil in 20 kg bags loaded after the furnace was at soil melting temperature. The maximum arc power during this test did not exceed 200 kW.

A partial analysis of the elemental composition of the Idaho soil used in this test is given in Table 3. Prior to furnace start up 200 mesh (74 μm screen spacing) sieved soil particulates were blown through the furnace mounted microwave plasma device and the threshold detection level for Cr was established to be comparable to the laboratory measurements. Also cold furnace start up arcing was observed to kick up soil dust particulates into the exhaust stream. For these initial measurements the plasma flame was orientated horizontally as shown in Figure 2.

Concern for the settling of debris in the plasma tube motivated a change of the plasma flame orientation to a vertically downward one before the high temperature furnace run. The plasma was less stable after this reconfiguration while the microwave device was at room temperature. However, once the furnace exhaust gases and the microwave plasma hardware became hot (> 300 °C) the plasma became very stable

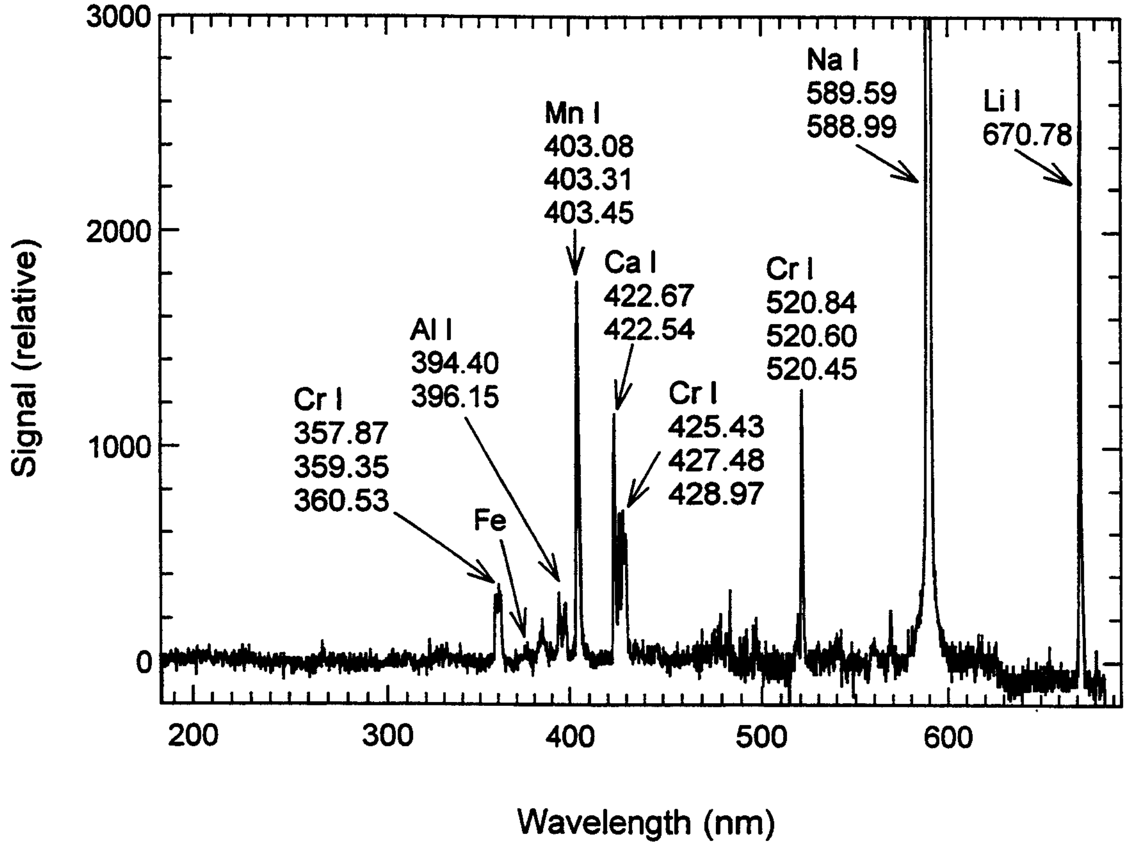

Figure 5. UV through visible emission spectrum taken with the low resolution spectrometers after the furnace was at soil melt temperatures but before additional soil loading.

with no tendency to go out even under extremely variable exhaust flow conditions. It was operated intermittently during furnace warm up and then continuously for a 49 hour period which included the soil loading and melting operations. The maximum temperatures monitored during this time period on the plasma input tube and graphite waveguide were 664 and 367 °C, respectively.

The plasma input pipe intercepted approximately 0.5% of the total furnace exhaust flow from the center of the 36 cm square furnace exhaust duct. Representative plasma spectra taken after the furnace was hot (> 1300 °C slag temperature) but before additional soil loading are shown in Figures 5 and 6. Figure 5 shows a complete uv through visible spectrum taken with the low resolution spectrometers and Figure 6 shows a high resolution spectrum of the chromium peaks near 359 nm. The signal integration times for both these spectra was 0.5 seconds.

Only metal emission lines are prominent in these spectra. All the metals that appear are present in the furnace soil fill, although aluminum and sodium are also known to be possible contaminants from the alumina tube at the base of the plasma. The relative emission intensities of these metals did evolve during the furnace operating

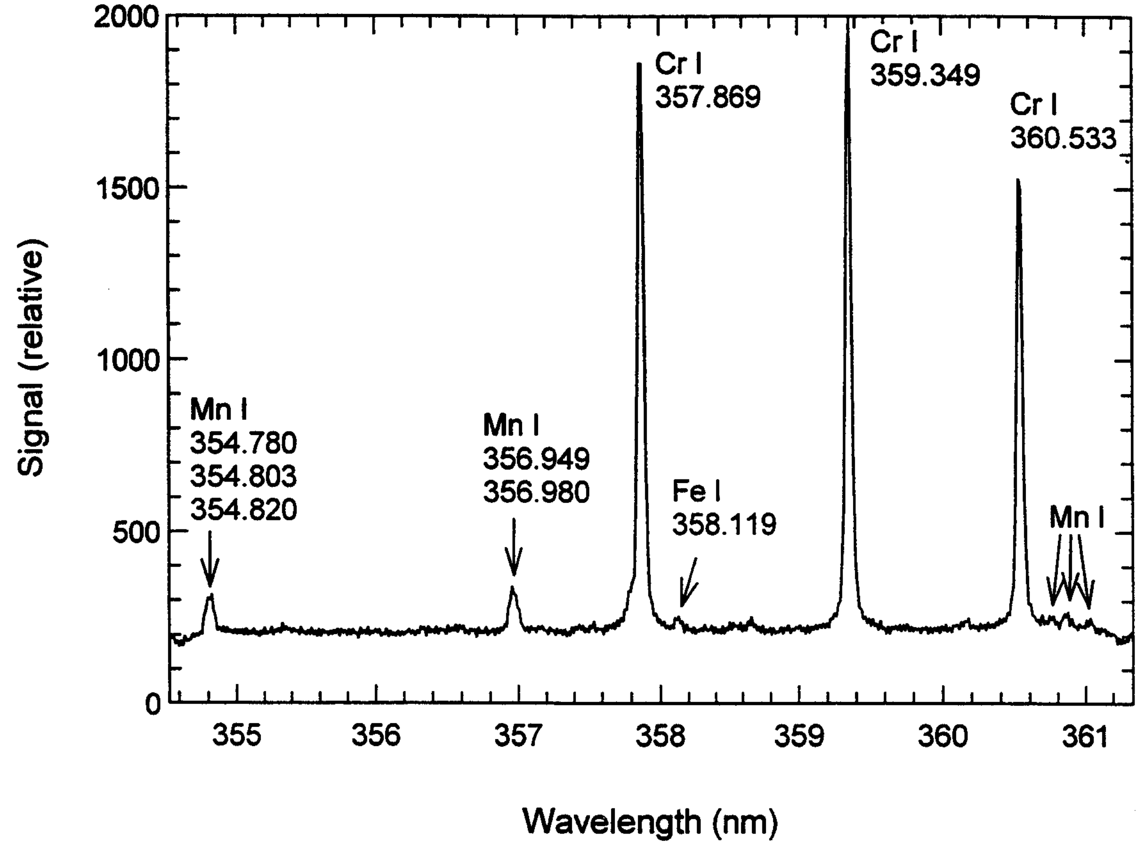

Figure 6. High resolution spectrum of the chromium emission near 359 nm for the same furnace conditions of Figure 5.

period with iron emission being dominant at start up. It is interesting to note that when the furnace is at temperature a trace component of the soil such as chromium is a major component of the exhaust while a major component in the soil such as iron is almost undetectable in the exhaust. This is indicative of the major role the slag chemistry must have in trapping or not trapping the various metals.

Another interesting observation is that there is no significant background emission from molecular species. This is somewhat unexpected since Mark II is arcing to graphite electrodes in a nitrogen purge, a condition that would seem likely to produce a gas matrix in which N_2^+ and CN bands would be present. Laboratory measurements did have interfering CN bands when graphite was present in the samples. The relatively clean background observed in the emission spectrum of actual furnace exhaust gas suggests that laboratory sensitivities could be achieved in a real time monitoring instrument.

High resolution spectra over the wavelength range of Figure 6 where recorded once every half second for much of the Mark II furnace test. Plots of the peak metals emission signals as a function of time clearly demonstrate the capability of the microwave plasma CEM for rapid real time hazardous metal measurements. This is illustrated in Figures 7 and 8.

A seven hour record overlapping the soil loading period is shown in Figure 7 for chromium emission and the simultaneous slag temperature taken with an active millimeter-wave pyrometer [15]. Chromium was the only metal in the EPA hazardous metals list that was observed to be continually present in this furnace test. Gaps in the chromium emission plot are due to lack of data storage at those times. Two general features of hazardous metal emission from a furnace are evident in this test. First, there are rapid transients in the emission which can be correlated with furnace feeding and changes in slag temperature. Second, the emissions, which are plotted on a logarithmic scale, vary over a dynamic range greater than three orders of magnitude. In fact, the signal was saturated near 10.5 hours at the start of furnace feed operations and between 14.8 and 15.1 hours just before furnace turn off.

In Figure 8 the time scale is expanded to a 70 minute period at the start up of soil loading including the loading of the first four bags. The simultaneous records for chromium, iron, and manganese emissions are shown demonstrating the multimetals capability of the microwave plasma CEM which is only limited by the spectrometer system to observe multiple transitions. Further insights into the furnace process are evident. Different metals can behave differently in the exhaust as is apparent for iron which differs from the chromium and manganese emissions. Also the double spikes in the emissions (most evident in the iron data for bags 3 and 4), one just before a bag is dropped in and another as it enters the slag, along with the general increase in metals emissions as the load chambers were readied before bag feeding suggest that there are two routes to metals emission in the exhaust. One route is from the slag and the second route is from dust blown directly from the furnace feed port into the exhaust.

The emissions data shown in Figures 7 and 8 is not quantitative. An approximate order of magnitude relationship between the signal levels and concentration can be estimated by assuming the hot furnace exhaust threshold detection level is comparable to the room temperature measurements and that the signal level is a linear function of concentration. In that case the chromium emission signal level of 10 in Figure 7, which is at about the threshold detection level for chromium in the exhaust, can be assigned to correspond to a concentration of approximately 2 $\mu g/m^3$ and the maximum signals in that plot to about 2 mg/m^3 (2 - 2000 ppb).

However, there are a number of factors that can effect this calibration. These include the effect of elevated temperatures in the exhaust environment, the variability in exhaust flow rate and matrix composition as the components of the soil feed are volatilized, and obscuration of the fiber optic view in the dirty exhaust flow. Degradation in light transmission in one of the three fibers used in the present test was observed, though with multiple fibers it is possible to identify this effect and correct the signal or replace the fiber. Accurately assigning metal concentrations to the detected signal levels will require real time calibration techniques which can function throughout the furnace operational range. Such a development will be the focus of future work.

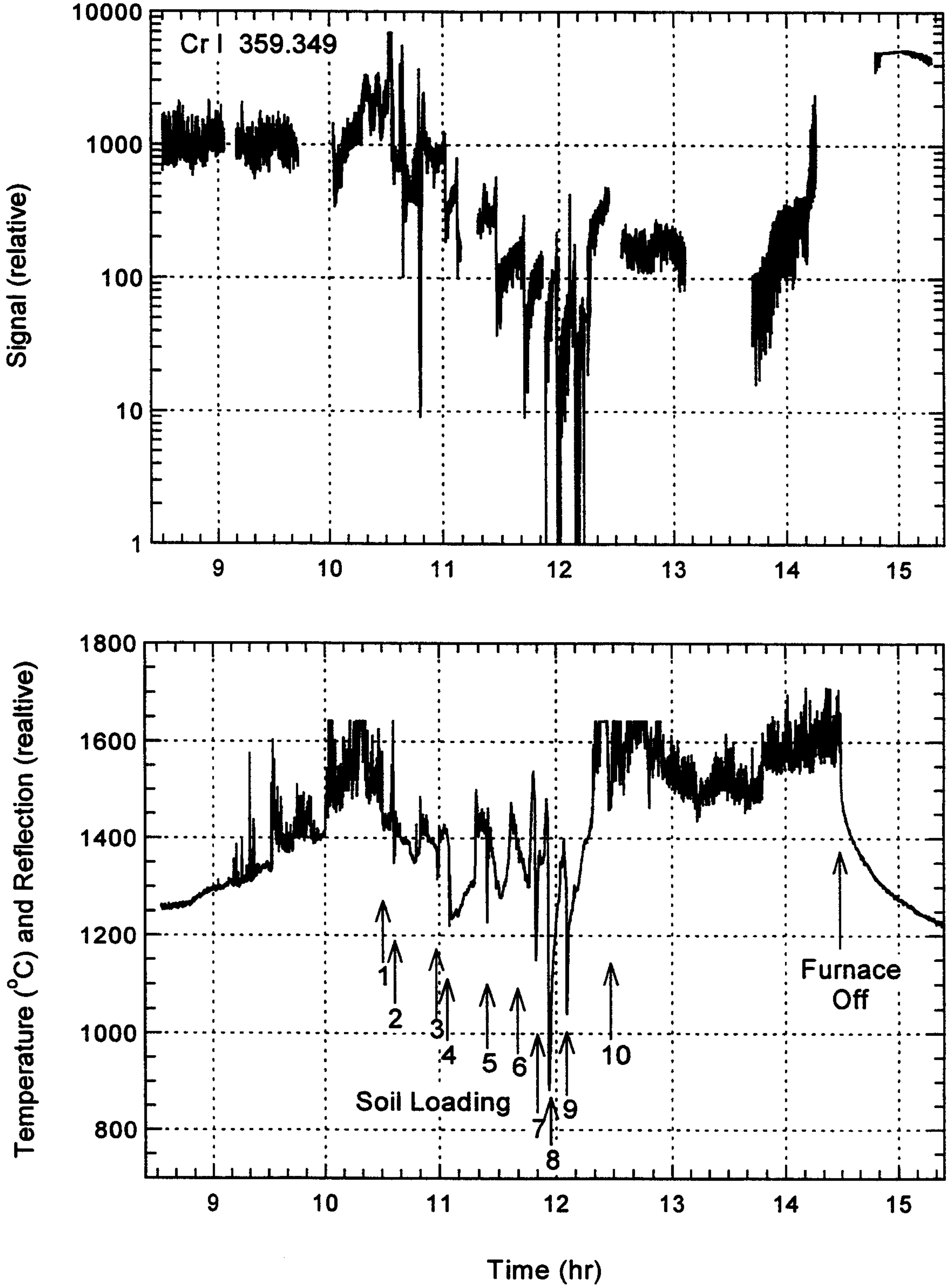

Figure 7. Chromium emission (top) and furnace slag temperature (bottom) for a seven hour period including the time when 10 soil bags were dropped into the slag as indicated by arrows in bottom plot.

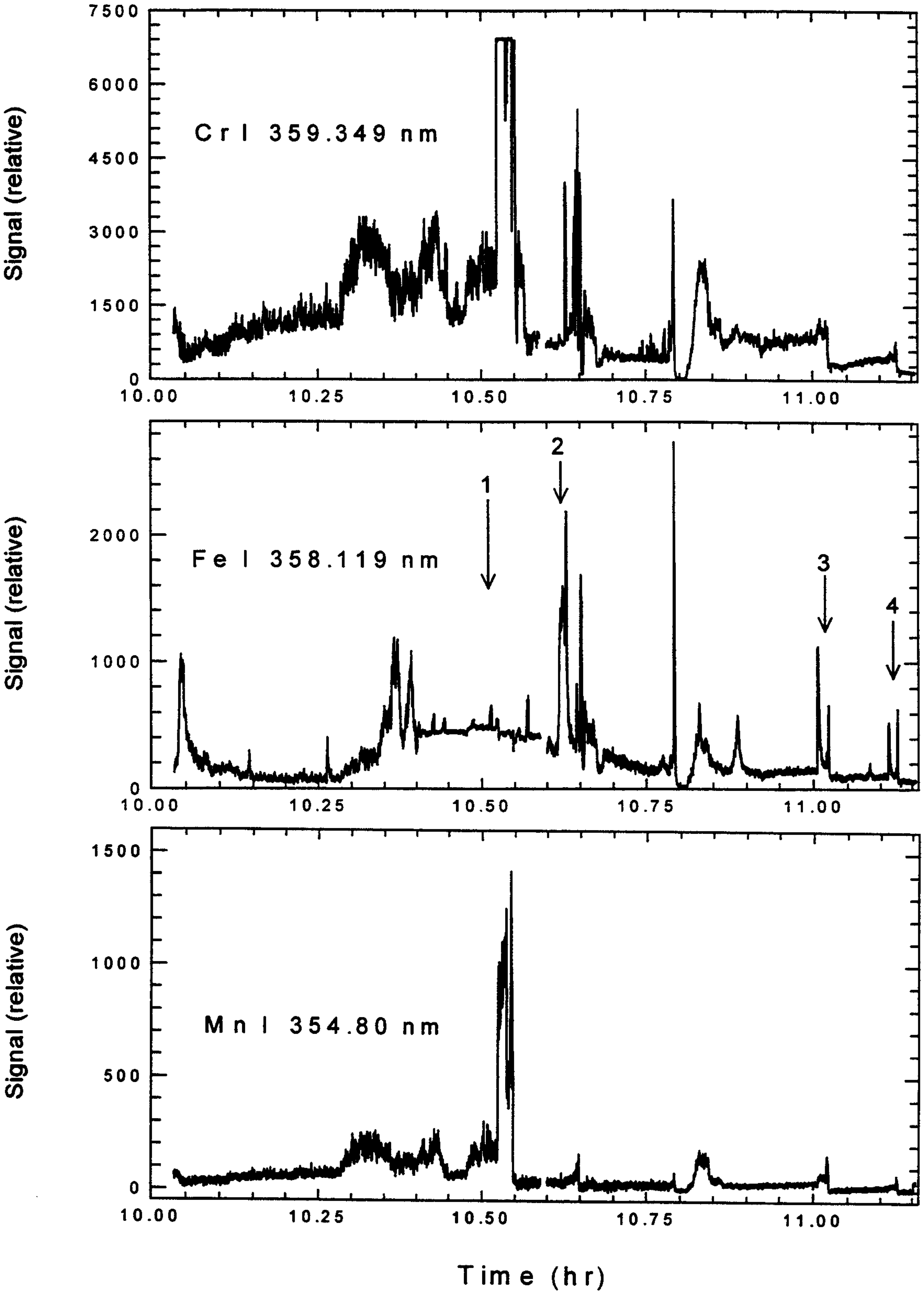

Figure 8. Simultaneous emissions of chromium, iron, and manganese for a 70 minute time period at the start up of furnace soil feeding. Times for drop in of bags 1 - 4 are indicated in the middle plot.

V. Discussion

The laboratory and furnace measurements have shown that a microwave plasma in a shorted waveguide structure constructed of refractrory materials and mountable into a furnace exhaust duct is a robust, comprehensive, and sensitive instrument for real time monitoring of metals entrained in furnace exhaust. In fact, the robustness of the microwave plasma in a high temperature furnace environment was found to improve relative to room temperature operation. In addition, background plasma light emission with undiluted furnace exhaust was found to be as low as in a laboratory setting making possible the achievement of laboratory metal detection sensitivities in a real time measurement environment. These features combined with the ability to sample directly large flow volumes comparable to EPA method 29 makes a microwave plasma CEM a very attractive choice for trace metals monitoring.

Another significant advantage is the capability of this instrument to directly sample hot undiluted furnace exhaust gas up stream of scrubbers. This provides significant signal leverage to monitor actual emissions discharged into the air at levels far below the threshold sensitivity of this device or any other device. This is because the threshold sensitivities can be divided by the efficiency of the scrubbers to remove metals. Furnace control for the prevention of hazardous metals pollution could be effectively carried out with a microwave plasma CEM for metal emission levels into the air that would be normally undetectable by any means.

Work is still needed to develop a real time calibration capability for this device. Such a development will be important if this device is to be used for compliance monitoring in the exhaust down stream of the scrubbers. However, even without a precise real time calibration capability the furnace measurements in this work demonstrate that this instrument can be quite useful. In its maiden test on a pilot scale arc furnace it has provided useful insights into the exhausts emissions processes of a furnace. Therefore, in its present form it can be a useful tool for development of and understanding of emissions in many applications using thermal processes. Also, precise calibration would not necessarily be a requirement in some control applications. The microwave plasma CEM as described here fills an important need for sensitive real time trace metals measurement instrumentation.

Acknowledgments

The assistance of Raul Valdez, Karyn Green, and Brian Pollack with the measurements is gratefully acknowledged. This work was supported by Battelle Pacific Northwest Laboratory as part of the Landfill Stabilization Focus Area, Office of Technology Developement, Environmental Management, U. S. Department Of Energy.

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