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**Detection of Plutonium with the Microwave Plasma
Continuous Emissions Monitor***

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* 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: The first successful detection of plutonium with a continuous microwave plasma emissions monitor has been demonstrated. Seven plutonium emission peaks in the 362 - 366 nm and 449 - 454 nm ranges were clearly observed. The strongest peak was at 453.62 nm. This peak and five of the other plutonium peaks were easily distinguishable from possible interference from iron emission peaks with a spectrometer resolution of 0.1 nm.

Introduction

The microwave continuous emissions monitor has been demonstrated in-situ on the Mark II DC arc furnace[1]. This device has proven to be a robust monitor for trace metals in a hot, undiluted stream of furnace exhaust gas. Successful detection of various metals (Fe, Cr, Mg, Mn, Ba, etc.) in real time has been accomplished. Techniques for calibration and quantification of detected metals are also currently being investigated. The ultimate goal of this program is the development of a DC arc furnace system, capable of processing radioactive mixed wastes, such as those found in landfills across the DOE complex. Many of the buried waste sites have mixtures of hazardous wastes containing heavy metals and radioactive species such as plutonium. Due to public concerns with emissions from DOE treatment activities, a need has been identified to develop a technique to monitor for trace levels of plutonium in the treatment off-gas. Presently no real-time plutonium measurement technique exists. Therefore, testing of the microwave plasma continuous emissions monitor for the detection of plutonium has been a critical development task under this program. As a part of the milestone requirements for the 1994-1995 period, experiments were conducted in the summer of 1995 at the Battelle Pacific Northwest Laboratories (PNL) in Richland, WA, to detect plutonium with the microwave plasma continuous emissions monitor

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Experimental Technique and Procedures

Experimental measurements were performed at PNL rather than at MIT because of the radiation safety requirements in handling plutonium. The experimental setup was similar to the laboratory setup at MIT (figure 1), with the exception of a fume hood surrounding the radiation area, and a condenser and HEPA filter to reduce plutonium release to the working area in the fume hood. An ASTEX 1.5 kW, 2.45 GHz microwave source was used to supply power to a shorted waveguide which generate the plasma in atmospheric pressure nitrogen gas flow. The plasma breakdown occurs a quarter wavelength from the shorted end of the rectangular waveguide with outside dimensions of 7.6 x 3.8 cm (WR284). The magnetron power was maintained at 600 W with 15 W reflected power. Nitrogen gas flowing at 30 SCFH was used to maintain the plasma. Because of the safety concerns about radiation contamination, the shorted waveguide exposed to plutonium contamination is inserted into the fume hood, and hence isolated. The rest of the experimental equipment was placed outside the fume hood, and not exposed to radioactive contaminants. A window separated the magnetron assembly from the plasma section to prevent radioactive contamination within the waveguide. All sample preparations and applications were done inside the fume hood with appropriate precautions taken for radiation safety.

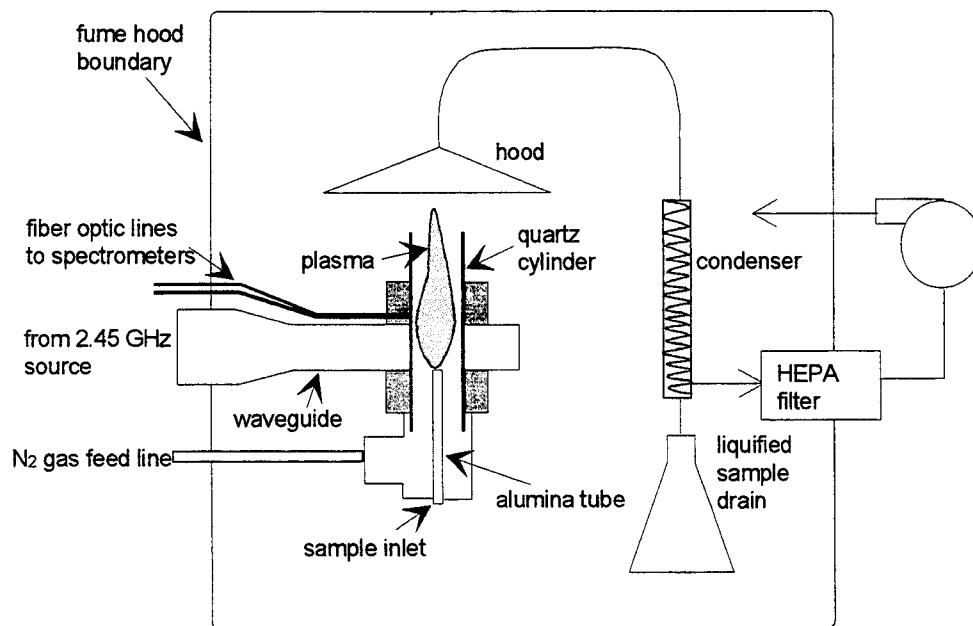


Figure 1: Experimental setup for plutonium measurements with the microwave wave continuous emissions monitor.

In order to minimize introducing plutonium to the fume hood environment, an additional filtration system was used in the exhaust end of the plasma (figure 1). A small fume hood covering the plasma was attached to a condenser to liquefy any vapor containing traces of

plutonium. A slight vacuum was created with a mechanical pump to draw plasma exhaust into the condenser and filtration system.

A fused quartz fiber optics system is attached to the shorted waveguide to allow remote spectroscopic analyses of plasma emissions. Two spectrometer systems were used in the experiment. A wide band Ocean Optics model SD1000 fiber optics spectrometer and a narrow band Chromex 500IS/SM Spectrograph/Monochromator were used to study atomic emission lines from the plasma. The Ocean Optics model has a 1200 lines/mm grating and a linear 1024 CCD array. This spectrometer has two channels, the first channel looks from 200 nm to 465 nm, and the second channel looks from 460 nm to 680 nm. This system has a resolution limit of about 1 nm. The Chromex model has user selectable 600/1200/2400 lines/mm gratings with 256 x 750 element CCD array. With the 2400 lines/mm grating, the resolution limit is about 0.1 nm with an instantaneous wavelength window of about 7 nm.

For this experiment, a solution of ultra high purity plutonium was used as a source to introduce plutonium to the plasma. Less than 20 μl of a solution having 0.04 gm/ml plutonium concentration (2470 $\mu\text{C/ml}$) was used for the entire experiment. For wavelength calibration purposes, a chromium solution of 10000 $\mu\text{g/ml}$ concentration in 5 % HNO_3 , and 99.9 % purity iron filings were also used as samples. Plutonium and the other calibration elements (chromium and iron) were introduced into the plasma by applying small amounts of either solutions or powders to the end of an alumina rod and inserting it into the plasma. The sample rods were inserted through the 3/8" OD alumina tube located at the input flow side of the waveguide. Clean alumina rods were used to introduce element samples to the plasma. To minimize cross contamination, separate rods were used for individual samples.

For this experiment, the primary goal was to test the feasibility of detection of plutonium. Precise quantification/calibration of observed lines was not possible because of the slow data acquisition electronics and transitory nature of sample introduction. Quantification and calibration of plutonium measurements will be performed in the future.

Experimental Results

Two 7 nm wavelength regions in the UV spectra, one centered on 365 nm and the other including 453 nm, were selected for the experimental observation of plutonium. These two regions were selected because they exhibited the strongest plutonium lines in ICP plasmas [2]. Since the microwave plasma parameters are similar to an ICP plasma, the selected regions hold the highest likelihood for the spectroscopic detection.

A total of 11 plutonium sample introduction runs were made into the plasma by dipping the end of an alumina rod into the plutonium solution and then inserting into the plasma. The fraction of the solution adsorbed by the alumina rod was not quantified. Both the Chromex and Ocean Optics spectrometers were used to acquire spectral data

simultaneously for each run. Since the Chromex spectrometer has a wavelength window of about 7 nm, a series of runs were made to first cover the regions from 353 nm to 373 nm and then from 445 nm to 460 nm.

Figure 2 shows the spectra in the 365 nm range, and figure 3 shows the spectrum in the 453 nm range. Spectra in both figures were acquired with the Chromex spectrometer. The 256x750 element CCD array was configured in software to run as a 1x750 element array by adding the signals in the 256 element columns. The spectra shown by dashed lines in figures 2 and 3 were acquired when iron filings were introduced into the plasma. The solid line spectra were acquired with the insertion of Pu solution into the plasma.

Small signatures of plutonium peaks were also present in the spectra acquired with the Ocean Optics spectrometer. Small peaks in the region of 450 nm were observable in the spectra, and are believed to be plutonium peaks (449.38 nm, 450.49 nm, and 453.62 nm). However, the Ocean Optics spectrometer's poor line resolution, and its large wavelength coverage which spans over 250 nm in each channel makes it difficult to identify each peak conclusively.

The strongest plutonium emission peak observed was at 453.62 nm and is shown in figure 3. Other plutonium lines were observed at 450.49 nm and 449.38 nm. With the Chromex spectrometer, the iron peak at 449.457 in figure 3 interferes with the plutonium peak at 449.381 nm, and it would be difficult to resolve this Pu peak in the presence of Fe impurities. However, the other two lines are clear of Fe interference.

Figure 2 shows four well resolved plutonium peaks (362.76 nm, 363.59/363.64 nm, 365.14 nm, 365.95 nm) and one peak that has a strong interference with Fe (363.22 nm). The resolution of the Chromex spectrometer was not high enough to resolve the two plutonium peaks at 363.59 nm and 363.645 nm, but this is not necessary for the detection of Pu.

For the two wavelength regimes analyzed, the best plutonium line to track is the peak at 453.62 nm. The next best plutonium lines are at 450.491 nm and 365.945 nm. These peaks are widely separated from other peaks, and even a spectrometer with only about 1 nm resolution should be able to resolve these peaks.

Conclusion

The first successful detection of plutonium lines with a microwave plasma continuous emissions monitor has been achieved. Plutonium emission lines in the 365 nm and 453 nm ranges were observed. Several plutonium peaks were clearly distinguishable, and interference effects from iron emissions were not significant for most of these peaks. More precise measurements of detection limits and techniques for calibration will be investigated in the future. However, previous measurements of detection limits for other heavy metals (Cr, Hg, Cd, etc.) have demonstrated sensitivities of less than one part per

billion with this monitoring device, and it would be expected that sensitivities to plutonium would be similar. This experiment verifies the viability of the microwave plasma continuous monitor to detect and track plutonium in furnaces for remediation of contaminated soils.

References:

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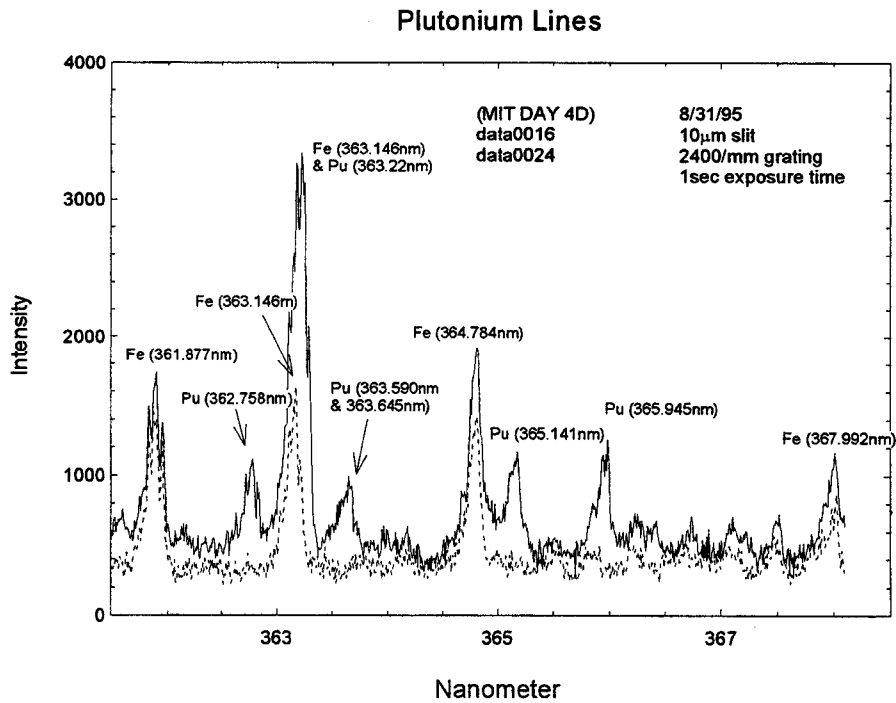


Figure 2: Iron and plutonium lines in the 365 nm wavelength range. Data acquired with the Chromex narrow band spectrometer.

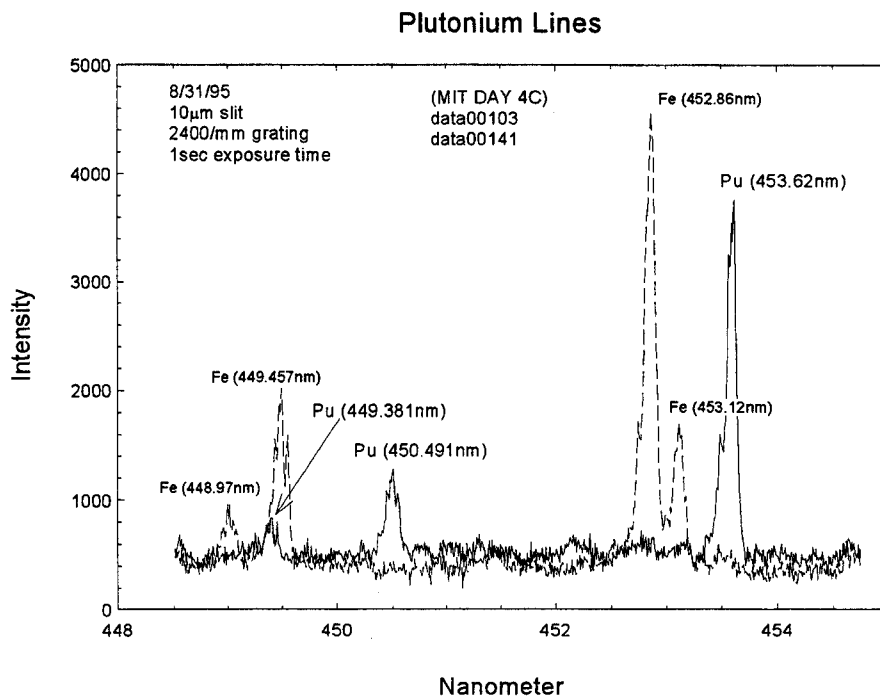


Figure 3: Iron and plutonium lines in the 453 nm wavelength range. Data acquired with the Chromex narrow band spectrometer.