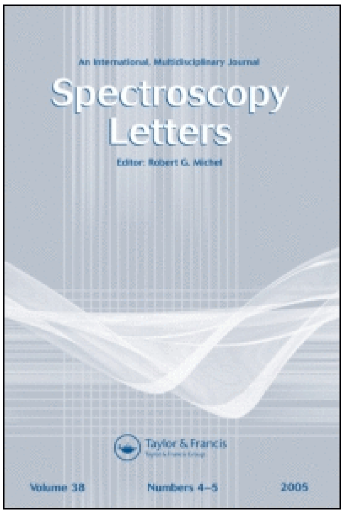

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Atomic Emission Spectrometry of Microsamples in a Glow Discharge

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ATOMIC EMISSION SPECTROMETRY OF MICROSAMPLES IN A GLOW DISCHARGE[a]

Key Words: Lead, Glow Discharge, Emission Spectroscopy

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ABSTRACT

A glow discharge system for atomic emission spectrometry is evaluated for physical and analytical characteristics. Lead (as the nitrate) is the model element used for these studies. The sputtering characteristics of several electrode designs are studied with the best system tried resulting in total sample vaporization in less than 1 s. Discharge currents up to 200 mA at a discharge voltage of 1200 V and a pressure of 2 torr are found to give the best results. The detection limit for lead is 0.9 ng and the linear dynamic range of response is greater than 2 orders of magnitude. Sodium chloride at a 100-fold excess amount causes a 50% decrease in the signal level.

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INTRODUCTION

Glow discharges have been used for analytical measurements in emission spectrometry[1,2,3,4,5,6] and to a lesser extent in absorption[7,8], fluorescence[9,10,11,12,13,14] and mass spectrometry[15,16,17]. They have been primarily applied to the analysis of trace elements in conducting solids, where an atomic vapor results from the sputtering process. Sputtering[1-5] has been found to result in fewer matrix effects than thermal vaporization in graphite furnaces. The reader is referred to several references for a discussion of principles,[16,18,19] instrumentation[1-15] and analytical uses[1-15] of glow discharges in atomic and mass spectrometry. In this study, we have evaluated the sputtering process and analytical figures of merit for small samples containing lead in a glow discharge with a cooled copper hollow cathode electrode. In order to achieve the best detection limits in glow discharge atomic emission spectrometry, it is necessary for the entire sample to be sputtered and excited within the shortest period of time. We have achieved complete sputtering/vaporization/excitation of small samples within a 1 s time period.

EXPERIMENTAL

A schematic diagram of the experimental setup is shown in Figure 1. Figure 2 shows the glow discharge chamber in more detail; it consisted of a six-way vacuum cross (Huntington Lab, Inc., Mountain View, CA) mounted on an X-Y-Z translation stage for optical alignment. Two of the ports were used for the cathode holder and for the introduction of the fill gas (Ar). The third port at 90° to the electrode port contained a vacuum gauge. Two other ports were used for the cathode holder and for the introduction of the fill gas (Ar). The sixth port contained a quartz window to allow measurement of the emission flux which was collected by a lens (7.5 in focal length) and focussed on the entrance slit of a monochromator (Model 218, f/5.3, 0.3 m McPherson with 1200 grooves/mm grating). The cathode holder-electrode assembly is shown in Figure 3. The cathode holder was constructed from a brass rod which was drilled out to allow water cooling of the electrode held in the end of the machined rod as shown in Figure 3. The rod was insulated from the glow discharge chamber (Figure 2) by means of a quartz sleeve which fit snugly over the cathode holder. A polymeric resin (Torr Seal, Varian, Lexington, MA) was used to seal the quartz sleeve to the cathode rod while maintaining vacuum. The sides of the copper cathode were protected by a ceramic sleeve.

The discharge was maintained by a high voltage power supply (Model 803-330, Hipotronics, Inc., Brewster, N.J.) which supplied voltages and currents up to 3000 V and 400

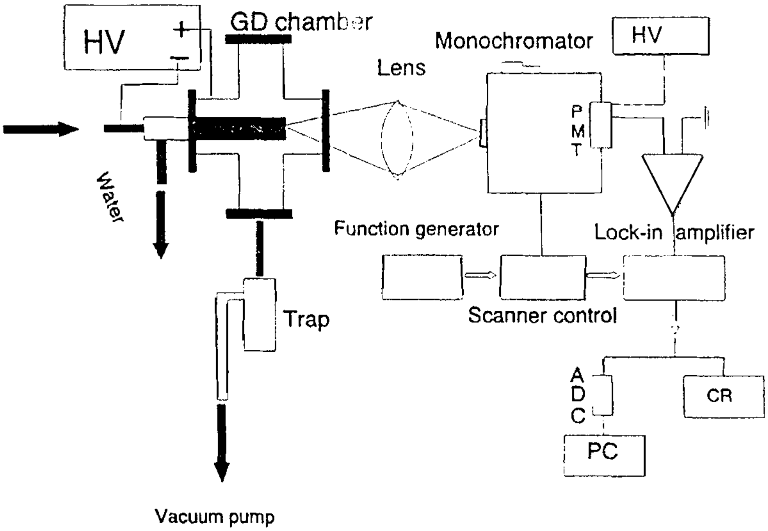

Figure 1. Schematic Diagram of Glow Discharge-Atomic Emission Spectrometric System.

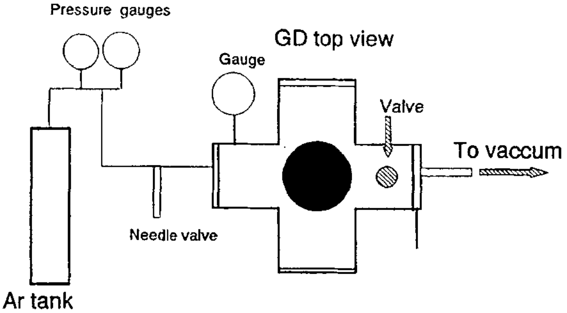

Figure 2. Schematic Diagram of Glow Discharge Chamber with Vacuum/Gas System.

mA, respectively. The stainless steel chamber was attached to the positive terminal and the cathode holder to the negative terminal. A 2.5 kΩ current limiting resistor was placed in series with the power supply.

Background correction was performed using an oscillating quartz plate (2.5 cm x 5.0 cm x 0.2 cm thick) behind the entrance slit of the monochromator. The plate was mounted

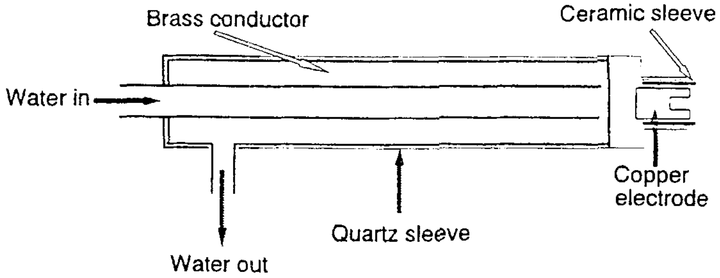

Figure 3. Schematic Diagram of Glow Discharge Copper Hollow Cathode Holder Assembly.

on the shaft of a rotating mechanical oscillator (General Scanners, Model G300PDT) mounted on the top of the monochromator; the frequency and angle of modulation were controlled by a signal generator (Wavetech Inc., Sunnyvale, CA) and a scanner control (Model CCX101, General Scanners, Inc., Watertown, MA). A lock-in amplifier (Model 5101, EG&G Princeton Applied Research, Princeton, NJ) was used for data acquisition. The oscillating plate was operated at 100 Hz with an angle of rotation of 5°. A wavelength interval of 0.45 nm was scanned. The emission flux passing through the monochromator exit slit was detected by a photomultiplier tube (Model R955, Hamamatsu Corp., Bridgewater, CT) operated at -950 V. The output current was amplified by a current-to-voltage converter (Model 427, Keithley Instruments, Inc., Cleveland, OH) prior to the lock-in amplifier. The lock-in signal was processed by an analog-to-digital converter (Model SR245, Stanford Research Systems, Palo Alto, CA) and stored in a personal computer for further processing.

The measurement procedure was as follows. The cathode holder was removed from the discharge chamber, the cathode removed, rinsed with 5% nitric acid and then ultrapure water and reinserted into the cathode holder. The holder was then inserted into the chamber and a preburn for 2-3 min was used to clean the cathode surface. The holder was then removed and the sample was added (usually 500 nL using a micropipette having a relative precision and accuracy of 5%) to the cathode. The cathode was placed inside the cathode holder, the ceramic sleeve was inserted and the chamber was evacuated to <0.1 torr for 2 min. The pressure was then set to the desired value by introducing Ar and the discharge was initiated by switching on the high voltage and the signal was recorded and stored. The 280.2 nm lead line resulted in the largest atomic emission signal-to-noise ratios (S/N); an interferant line at the 283.3 nm lead line prevented its use.

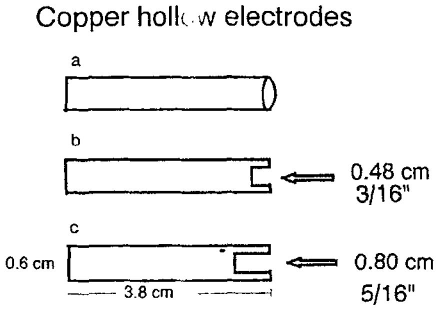

Figure 4. Diagram of Planar (a) and Hollow (b,c) Cathode Copper Electrode.

RESULTS AND DISCUSSION

The major emphasis in the study was the evaluation of the sputtering temporal profiles of small samples placed in/on the hollow cathode electrode. Although several types of hollow cathode materials, including pyrolytically coated graphite cups, platinum cups and platinum deposited graphite cups were evaluated, high purity copper electrodes were found to be superior in terms of lifetime and/or porosity. Three copper electrode types (see Figure 4) were evaluated. All electrodes were 6 mm in diameter. The cup depth was either 5 mm or 8 mm. The deeper cup electrode allowed higher discharge currents (> 150 mA) to be used.

The planar electrode glow discharge was stable with currents lower than 20 mA and pressures of 1-10 torr. However, no significant Pb emission was observed. Using the hollow copper cathodes (see Figure 4), intense Pb emission lines were observed.

The temporal profiles for 2 μg Pb added to the 5 mm deep cup and for three discharge currents are shown in Figure 5. A discharge pressure of 6 torr was found to give the best signal-to-noise ratio. It is clear that an increase in discharge current results in an increased lead emission signal. However, all attempts to work at higher currents were unsuccessful because of arcing problems. Therefore, all further studies were performed with the 8 mm deep copper hollow cathode which could be operated at currents as high as 200 mA and a potential of 1300 V without causing any plasma instability problems.

With a current of 190 mA and a voltage of 1200 V, the signal-to-noise ratio was maximal between 2-3 torr. The plasma became unstable at 1 torr and below and the emission signal fell linearly at pressures between 3 and 10 torr. A pressure of 2 torr was

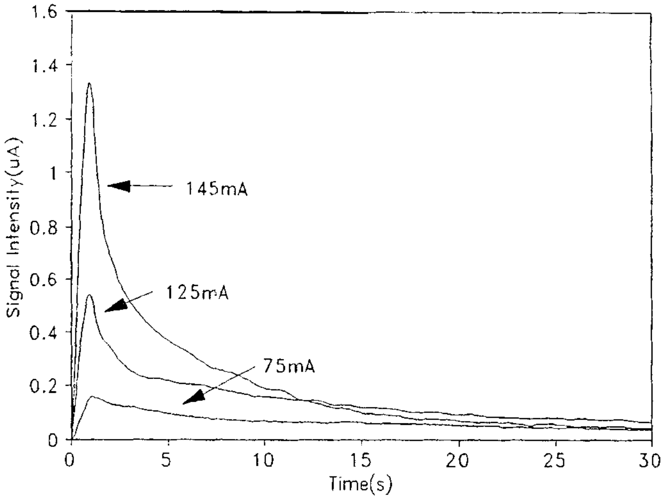

Figure 5. Temporal Behavior of Lead Atomic Emission at Three Discharge Currents (λ = 280.2 nm; Pb mass = 2 μg; discharge pressure = 6 torr, Electrode Cup Depth = 5 mm.)

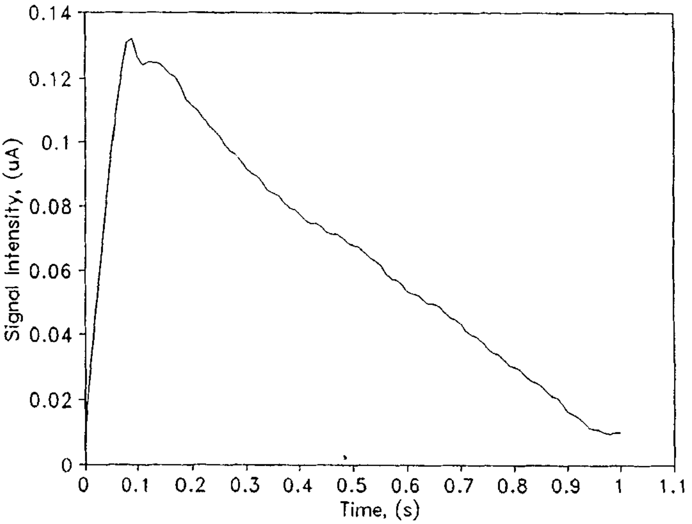

Figure 6. Temporal Behavior of Lead Atomic Emission (λ = 280.2 nm; Pb mass = 50 ng; Pressure = 2 torr; Electrode depth = 8 mm).

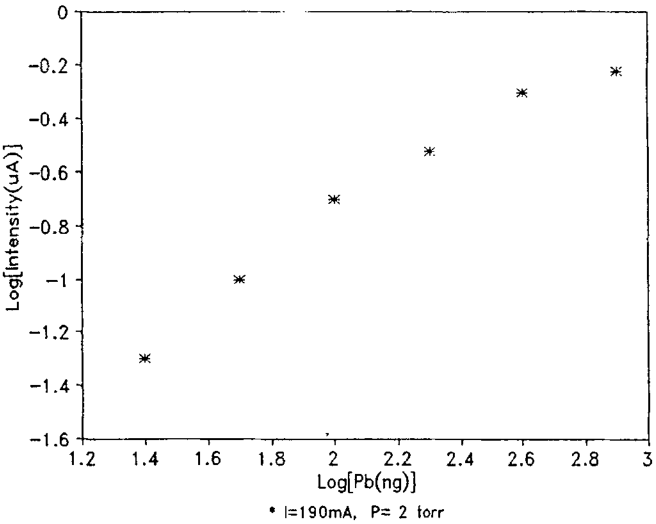

Figure 7. Analytical Calibration (Log-Log) Curve for Lead Atomic Emission (λ =280.2 nm; Discharge Current = 190 mA; Pressure = 2 torr; Electrode Cup Depth = 8 mm).

chosen for all further studies with the 8 mm deep copper cathode. In Figure 6, the temporal profile of a 50 ng Pb is given. The Pb was sputtered from the 8 mm cup in less than one second and the maximum emission signal was reached in approximately 0.1 s. The rise, fall and width of the temporal peak was largely determined by the instrumental time constant. An analytical calibration curve for lead is given in Figure 7. Multiple measurements (3 or more) were made for each point with a precision of 7-20 % RSD. The calibration curve had a log-log slope of 1.0 for the smaller masses with a linear dynamic range of at least 10^2. At Pb amounts above 400 ng, the calibration curve became non-linear. The detection limit (S/N =3) for Pb was 0.9 ng.

The influence of NaCl upon the Pb emission signal was also evaluated. A 50 ng Pb sample in the presence of 5000 ng NaCl resulted in a 50% decrease in the Pb emission signal, compared to 50 ng Pb with no NaCl present. Based upon atomic fluorescence measurements of Pb in the presence of NaCl, the decrease was most likely a result of a decreased sputtering rate.

Gallium was also briefly studied using the GD-AES approach. An analytical calibration curve with a log-log slope of 1.0 over a range of more than 100 fold and a detection limit (S/N=3) of 300 pg were obtained. The Ga 287.4 nm atomic emission line was used for the studies.

CONCLUSIONS

A novel glow discharge atomic emission spectrometric system has been evaluated. These initial studies indicate that this plasma is capable of sub-nanogram detection limits linear response and good precision. With future work involving new cathode types, such as glassy carbon, it should be possible to improve the analytical figures of merit. The presence of a lead blank in the present copper cathode limited the detection limit of lead.

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