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Direct, Continuous Hydride Generation Coupled with Microwave Induced Plasma-Atomic Emission Spectrometry for the Determination of Selenium

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**DIRECT, CONTINUOUS HYDRIDE GENERATION COUPLED WITH
MICROWAVE INDUCED PLASMA-ATOMIC EMISSION
SPECTROMETRY FOR THE DETERMINATION OF SELENIUM**

KEYWORDS: Microwave Induced Plasma, Hydride Generation, Atomic Emission Spectrometry, Selenium Detection.

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ABSTRACT

Selenium is determined by atomic emission technique with microwave induced helium plasma as the excitation source. A continuous hydride generation system using a peristaltic pump, an effective serpentine hydride generator and a gas-liquid separator is developed and interfaced to the He-plasma. The

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selenium hydride and the reaction by-products are carried directly and continuously by the He carrier gas (0.6 L/min) into the plasma sustained in a tangential torch. The power level is 100 W and the tangential helium flow-rate is 4.5 L/min. The detection limit (3σ) is 40 ppb, the linear dynamic range is over three orders of magnitude, and the precision is 6.7% RSD for a 1 ppm solution. Applications to a soil sample showed comparable results to a conventional hydride generation atomic absorption system.

Hydride generation (HG) has been used for sample introduction into microwave induced plasma (MIP). By using the HG technique, analytes are separated and concentrated into the gas phase, and therefore the detection sensitivity is much increased. Robbins and Caruso (1), and Nakahara (2) have reviewed HG for sample introduction in atomic spectroscopy. The HG reaction by-products such as hydrogen, carbon dioxide, hydrogen chloride and water, can easily extinguish the plasma if introduced directly into the MIP. Therefore, a common procedure is to couple the MIP with a cold trap and/or a gas chromatograph (GC)(1-4), allowing only the analyte hydrides to enter the plasma. Recently this laboratory succeeded in the use of a tangential torch (5) for direct, continuous HG into the MIP for the determination of lead (6). No separation or venting of hydrogen and other hydride reaction by-products were used. Direct, continuous HG is attractive because the system is simple to operate and can be easily automated.

This paper reports a direct continuous generation system for selenium hydride into an MIP. The system is similar to the one reported earlier (6) except that an improved serpentine reactor (mixing coil) and gas-liquid separator are used.

EXPERIMENTAL

A block diagram of instrumentation for the direct,

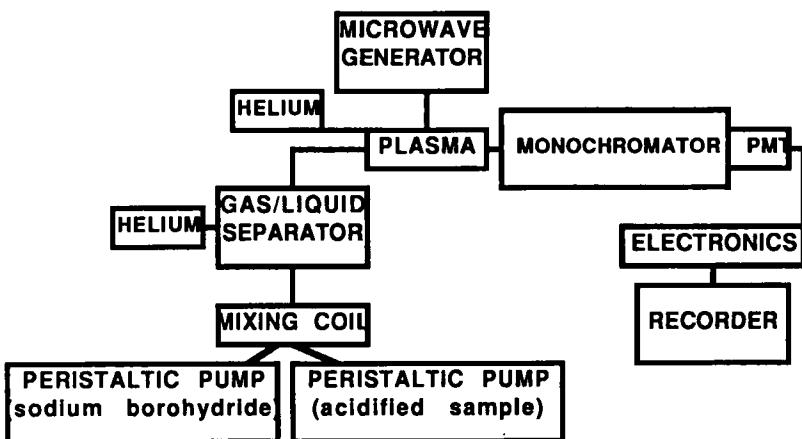


Figure 1. Block diagram of instrumentation.

continuous hydride generation, microwave induced plasma atomic emission spectrometric system is shown in Figure 1.

The MIP Spectrometer

The torch (5), microwave cavity (Beenakker TM010), microwave generator, tuner, monochromator, and electronics were of those reported (6) earlier; except that the focusing bi-convex lens was quartz (diameter 2.5 cm; focal length 9.95 cm), and the Pyrex sample injection tube of the torch had 7 mm o.d. and 2 mm orifice.

The Hydride Generator

The mixing coil (PTFE tubing: 1.2 mm i.d., 3 mm o.d., 15 X 5 cm 1/4 inch mesh screen) was constructed with the serpentine pattern as described by Curtis and Shawan (7). The gas-liquid separator (Figure 2) was constructed with Pyrex. The ISCO multichannel peristaltic pump (Silicone tubing: 3 mm i.d.; 6.5 mm o.d.) was used to deliver sodium borohydride solutions, and the Cole-Palmer single channel peristaltic pump (Tygon tubing: 0.8 mm i.d.; 3 mm o.d.) was used to deliver the acidified sample solutions.

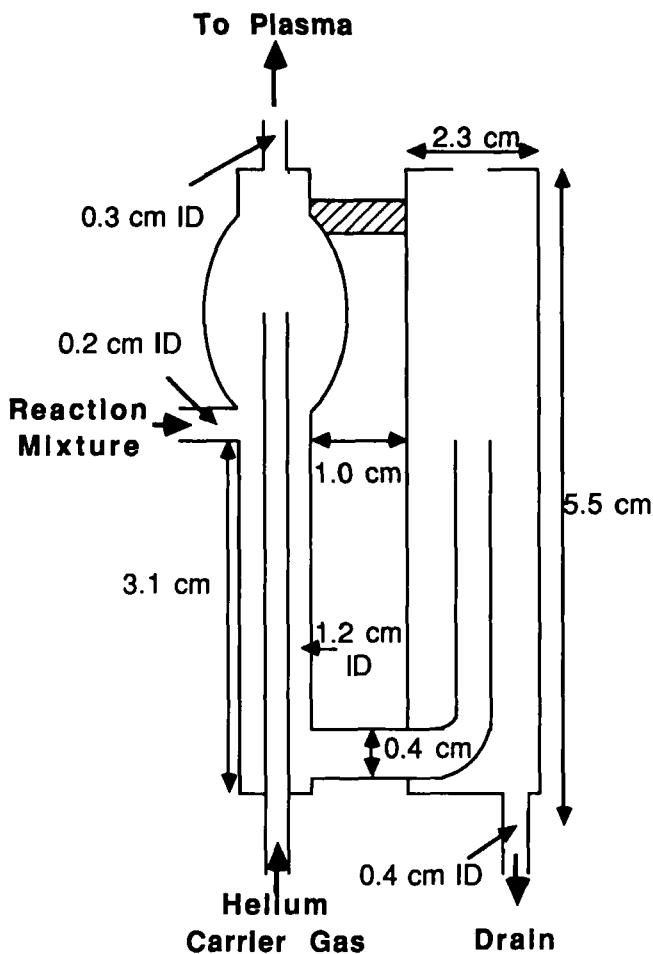


Figure 2. The gas - liquid separator used with the direct, continuous hydride generation MIP system.

Reagents

Solutions were prepared from high-purity deionized water that was produced by passing distilled water through a deionizing system (Barnstead, Division of SYBRON Co., Boston, MA). Other reagents used in these experiments were analytical grade unless specified. Selenium stock solution was made by

dissolving selenium dioxide (Spectrum Chemical MFG Corp.) in the deionized distilled water. The sodium borohydride solutions was made by dissolving sodium borohydride (Spectrum Chemical MFG Corp.) in 1% (w/v) sodium hydroxide solution, and was prepared fresh before use.

Soil Digestion

Soil samples were ground and sieved using a 110 mesh screen. Next, 2.5 mL deionized distilled water and 2.5 mL 70% nitric acid were added to 0.25 g soil in a digestion tube. A small funnel was placed on top of the digestion tube and the tube was placed in a digestion block and heated at 85°C for at least 12 hours. Then, 1.5 mL 30% hydrogen peroxide was added to the sample and it was heated for an additional 4 to 6 hours. Next, 18 mL of concentrated HCl was added and the sample then was heated at 85°C for a minimum of 12 hours. The sample was cooled and diluted to 50 mL with deionized distilled water. The sample digestion tube was covered and stored in a refrigerator until analysis.

Procedure

The tangential plasma helium gas was adjusted to 2-5 L/min for ignition at maximum power with a copper wire, and was adjusted to approximately 10 L/ min to center the plasma. Once the plasma was centered, the tangential helium gas was adjusted to 4.5 L/ min. and the plasma remained centered. The plasma was maintained at 100 W forward power (this is the highest power achievable with the torch although the generator is capable of 120 W maximum output). The peristaltic pump flow rates were increased gradually to the desired levels and the reflected powers were retuned to a minimum (< 2 W) during the process. The solutions were mixed well in the mixing coil and entered the gas-liquid separator where the helium carrier gas (0.6 L/min) transferred the gaseous products *directly* into the plasma. The spectrometer was

adjusted to 196.0 nm for monitoring the emission intensity of selenium.

RESULTS AND DISCUSSION

The detailed construction of the torch (5) used in this study and its mounting to the Beenakker MIP cavity (6), have been published. Argon plasma could be generated with the torch and centered easily for a variety of argon flow rates. However, the plasma was extinguished when the forward power was greater than 50 W. Because of the low forward power, the plasma was extinguished when a small amount of hydride generation product was injected into it. Helium plasma, however, was centered and stable at a power range from 50 - 100 W with the reflected power below 2 W. Helium plasma was used for further evaluation. It is interesting to note that when hydrogen from HG reaction is introduced into the helium plasma, the plasma is "absorbed" in the power region and the plasma is audibly quieter.

Optimization of Hydride Generation and Plasma Operation Conditions

Sample Acidity. It was found that 3-5 M (11-18%) was the most suitable concentration range of hydrochloric acid (Figure 3) on 10 ppm selenium detection.

Solution Flow Rates. When the sodium borohydride solution (1%) flow rate was 2 mL/min, increasing the sample flow-rate increased the signal intensity (Figure 3). At flow rates greater than 6.0 mL/min, however, the plasma was extinguished. The final optimized flow-rates were 6.0 mL/min in selenium sample solution and 1.8 mL/min in sodium borohydride solution.

Reagent Concentration. The concentration of sodium borohydride solution was investigated. The plasma was extinguished at a level of greater than 2%. The best signal to noise was at 1% and was adopted for operation.

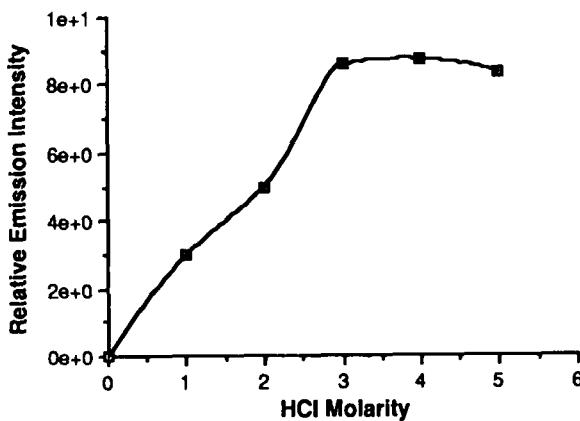


Figure 3. Effect of sample acidity on selenium sensitivity with the direct, continuous hydride generation MIP system.

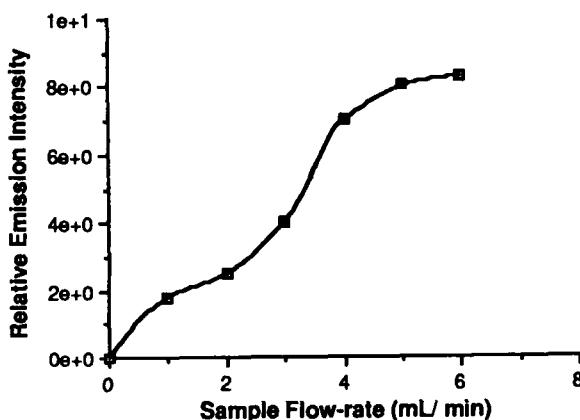


Figure 4. Effect of sample flow-rate on selenium sensitivity with the direct, continuous hydride generation MIP system.

Table 1

Operation condition for the direct, continuous selenium hydride generation microwave induced plasma atomic emission system.

Plasma forward power	100 W
Plasma reflected power	< 2 W
Plasma viewing mode	axial
Tangential helium flow	4.5 L/min
Sample carrier gas flow	0.6 L/min
Sodium borohydride concentration	1.1%
Sodium borohydride solution pumping rate	1.8 mL/min
Hydrochloric acid concentration	3 M (11%)
Sample solution pumping rate	6.0 mL/min
Slit Widths	35 μ m
Wavelength	196.0 nm
PMT power	1.1 kV

Carrier Gas. The use of helium carrier gas had decreased the noise level, decreased the memory effect, and increased the signal precision when compared to those without using the carrier gas. The optimized flow-rate was found to be 0.6 L/min. Lower than 0.6 L/min had created higher plasma background noise. Higher than 0.8 L/min caused high gas pressure inside the gas-liquid separator which pushed the liquid out of the inner tube, resulting escape of hydride generation products. The 0.6 L/min was used.

Tangential Support Gas. The lowest helium gas flow to keep a centered, stable plasma was 4.5 L/min. To minimize gas consumption, no analytical evaluations were done at higher flow rates.

MIP Power. The plasma could be maintained at a level of greater than 70 W forward power. The higher the applied

power, the higher the signal-to-noise. The highest power obtainable with the system was 100 W and was used in all investigations. The reflected power was less than 2 W during the HG-MIP operation.

The optimized parameters and other operating conditions are shown in Table 1.

Analytical Figures of Merit

Detection Limit, Linearity, and Precision. The detection limit was defined as analyte concentration that gave a signal equivalent to three times the standard deviation (3σ) when the blank hydride was generated, and was found to be 40 ppb. The linearity for the concentrations investigated is shown in Figure 5. It can be seen that the linear dynamic range is over three orders of magnitude. The signal precision computed from at least five runs of a 1 ppm solution showed a relative standard deviation of 6.7%.

The figures of merit of this system are compared to those of a HG(with cold trap)-GC-MIP system (4) in Table 2. Since there are no other direct continuous HG-MIP available, comparing this system to the others is difficult. This system is inferior in terms of detection limit and signal precision, but superior in the linear dynamic range.

Soil Analysis

The same soil digests were analyzed for selenium by using a conventional hydride generation with flame heated quartz cell atomic absorption system, and by using this system. The obtained results are shown in Table 3 and the numbers are virtually the same.

It is well recognized that the MIP is less tolerant to matrix effects when compared with other plasma sources such as the inductively coupled plasma and the direct current plasma. Its

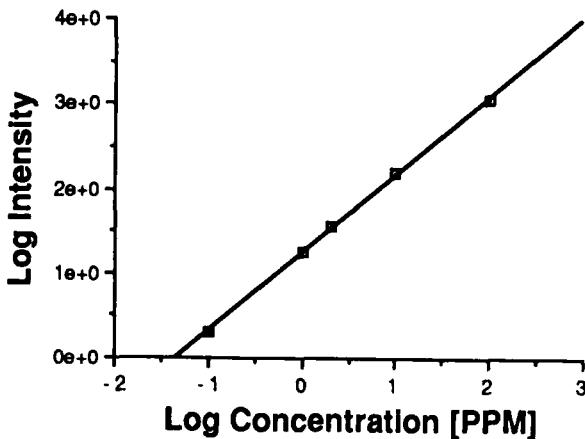


Figure 5. Linearity response for selenium using the direct, continuous hydride generation MIP system.

Table 2

Comparison of analytical figures of merit from two MIP systems for selenium detection at 196.0 nm.

<u>System</u>	<u>Detection Limit (3σ), ppb</u>	<u>Linear Range</u>	<u>Rel. Std. dev., %</u>
*Hydride Generation with Cold Trap -Gas Chromatography-			
MIP	2	5 - 500	5.5 at 0.05 ppm
Direct, Continuous Hydride Generation - MIP (this system)	40	10 ² - 10 ⁵	6.7 at 1 ppm

* Data taken from ref. 4. The concentration values have been corrected for a 20 mL sample volume.

Table 3
Soil Analysis for Selenium

<u>System used</u>	<u>Concentration</u> <u>Found</u> (PPM)
Direct, Continuous	
Hydride Generation-Atomic Absorption (with a flame heated quartz cell)	0.30 +/- 0.01
Direct, Continuous	
Hydride Generation-Plasma Atomic Emission (this system)	0.29 +/- 0.03

use as an excitation source is most successful for gaseous samples and when coupled with a sample separation procedure, namely gas chromatography or hydride generation. The previous report (6) and this paper clearly demonstrate the feasibility of direct, continuous hydride generation MIP systems. The current system operates at 100 W power and 5 L/min helium. We believe that the analytical figures of merit can be improved by applying higher power levels. Furthermore, the gas consumption rate should be reduced in order to make the system more attractive when compared to the other plasma systems.

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