Utilization of a Palladium-Coated Platform and a Methane/Argon Purge Gas Mixture in the Determination of Silicon by Electrothermal Atomic Absorption Spectrometry

Michael Hackney,† John Springfield,† Marcus Steele,*,† and Dennis Elmore‡

Department of Physical Sciences, Delta State University, Cleveland, Mississippi 38733, and Application and Production Technology Research Unit, Agricultural Research Service, U.S. Department of Agriculture, Stoneville, Mississippi 38776

An electrothermal atomic absorption spectrometric procedure to improve the analytical performance of determination of silicon in an aqueous matrix is discussed. The method employs a Pd sputter-coated L'vov platform and an argon/methane purge gas mixture. The use of this combination improved peak sharpness, precision, and calibration accuracy. RSD values were consistently under 5% and the linear dynamic range obtained using this procedure extended from 5 to 100 ng/mL. Calibration curves consistently had correlation coefficients above 0.999 and exhibited a detection limit of 1.1 ng/mL. The characteristic mass achieved during analysis averaged 35 pg/0.0044 A-s.

Keywords: *Silicon; ETAAS; alternative purge gas; Pd-coated L'vov platform*

Leaf surfaces are the primary locations for the administration of pesticides (whether fungicide, insecticide, or herbicide) in plants postemergent. Studies of pesticide application have shown that surfactants have a major influence on the deposition, spread, and retention of spray droplets (Gaskin and Stevens, 1993; McWhorter et al., 1995). These factors are affected by the microroughness and chemical composition of the leaf's surface. Microroughness affects the air/liquid and liquid/solid interfaces that in turn affect the pesticide incorporation into the cuticle (Boize et al., 1976). The major factors influencing the chemical nature of the leaf surface are the cuticle and the epicuticular wax. These have been examined previously in one plant species chemically and microscopically (Chambers et al., 1993; McWhorter et al., 1990). However, within this cuticle and epicuticular wax are some inclusions of silicon of an undefined nature (both quantitatively and qualitatively; McWhorter et al., 1995). We are interested in pursuing the nature and extent of these silicon inclusions. To do this requires a sensitive method of silicon analysis.

Electrothermal atomic absorption spectrometry (ETAAS) is the preferred method of measuring silicon at the parts per billion level. However, the accurate determination of carbide- and oxide-forming elements such as silicon is one of the more challenging types of ETAAS analyses. The silicon oxide and silicon carbide formed severely attenuate the Si signal and are presumably responsible for the bimodal absorption signal (Schleisman and Bollinger, 1995). Since the vaporization temperature of silicon carbide is 2800 °C, the atomization of pre-existing carbides is incomplete, causing reduced and/or changing sensitivity, changing baseline, and memory peaks (Nater and Burau, 1989; Rademeyer and Vermaak, 1992).

Historically, several procedures have been pursued in an attempt to improve the analysis. It has been reported that the use of Nb- and Zr-coated tubes (Muller-Vogt and Wendl, 1981), N_2 in place of Ar as the purge gas (Frech and Cedergren, 1980), and alkali metal fluoride matrix modifiers enhanced and stabilized the Si signal.

Recently, Sturgeon and others (Sturgeon et al., 1989) have experimented with the use of the graphite furnace as a trapping and preconcentrating medium of hydride-forming elements prior to analysis by atomic absorption or inductively coupled plasma (ICP). The hydrides are formed externally and introduced into the furnace in an Ar gas stream at relatively low temperatures (200−600 °C) and adsorb onto the graphite or the metal-coated surface. Subsequently, the furnace temperature is raised to 2000−2600 °C, the analytes desorb from the surface, and their concentration is measured immediately in the case of ETAAS or later as they are swept into the ICP. Significant improvement in detection limits for a number of elements has been accomplished using this technique.

Other researchers have examined the use of an alternative purge gas or gas mixture during the drying and pyrolysis steps to improve peak shapes and/or sensitivity of Sn (O_2/Ar) (Rademeyer and Vermaak, 1992), Se (H_2) (Mahmood et al., 1995), and Si (CH_4/Ar) (Schleisman and Bollinger, 1995). In each case the peak profiles are improved and sharpened and the detection limits are improved.

This study combines key elements of these two approaches. It uses a Pd-coated L'vov platform and an alternative purge gas to measure low levels of silicon in aqueous solutions.

MATERIALS AND METHODS

Apparatus. A Perkin-Elmer (PE) Zeeman/5100 atomic absorption spectrophotometer equipped with a Perkin-Elmer HGA-600 graphite furnace and a Perkin-Elmer AS-60 autosampler (The Perkin-Elmer Corp., Norwalk, CT) and controlled by a Dell 486 microcomputer (Dell Computers, Austin, TX) was used for this study. Argon was used as the primary purge gas at a flow rate of 300 mL/min, and the internal flow was stopped during atomization. An alternative purge gas composed of 95% Ar and 5% CH_4 was implemented during the drying and ashing steps of furnace operation. The slit width was 0.2 nm, and all measurements were made using the 251.6 nm line of Si. A Perkin-Elmer Si hollow cathode lamp was

† Delta State University.
‡ U.S. Department of Agriculture.

S0021-8561(96)00873-4 CCC: $14.00 © 1997 American Chemical Society

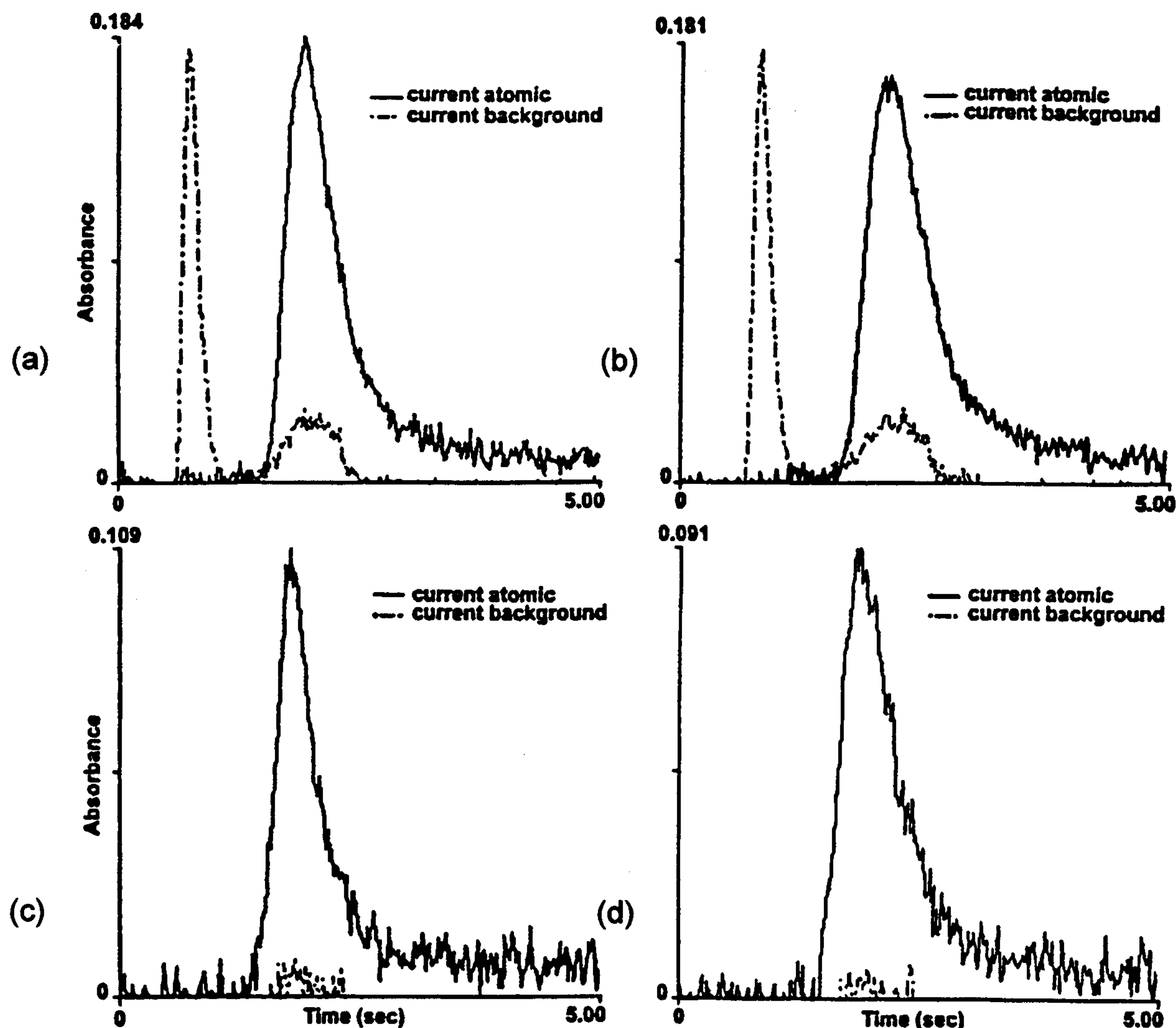

Figure 1. Atomization profiles obtained from a 40 μL aliquot of a 20 ng/L standard (a) with a Pd-coated platform and Ar/CH_4 purge gas, (b) with Ar/CH_4 only, (c) with a Pd-coated platform only, and (d) without a Pd-coated platform or Ar/CH_4 purge gas.

used as the light source and was operated at its recommended maximum, 40 mA. Pyrolytic coated graphite tubes (The Perkin-Elmer Corp.) fitted with a L'vov platform sputter-coated with 120 nm Pd were used. The operation and data handling of the PE/Z 5100 was performed using PE's 3.1 GEM software. The L'vov platforms were sputter-coated with a Hummer X sputter coater (Anatech, Ltd., Alexandria, VA).

Reagents. All of the standards were prepared from a stock standard of 1000 μg/mL silicon (Perkin-Elmer). Dilutions were made using water from a reverse osmosis/ion exchange ultrapure water system. The water purified by reverse osmosis is passed through a Nanopure II 4 Module water system (Barnstead-Thermolyne, Dubuque, IA). All solutions were prepared in polyethylene containers that had previously been filled with a 10% HNO_3 solution overnight. The spiked samples were prepared as were the calibration standards with the exception of the use of reverse osmosis water (ROW) as the diluent. Fresh solutions were prepared daily to ensure validity of data and to reduce the effect of silicon contamination from external sources. Calibration curves were run daily, and new polyethylene sample cups containing "fresh" standards were used each time a curve was established. This was done to prevent leaching of impurities from the polyethylene containers or cups to the standards, which can occur in a short period.

Procedure. Prior to Pd coating, each L'vov platform was cleaned by emersion in a 10% solution of trace metal grade HNO_3 (Fisher, Pittsburgh, PA) for at least 1 h. It was then dried in an oven (100 °C) for 1 h and exposed to a high vacuum (inside a scanning electron microscope sample chamber) overnight to remove adsorbed gases. The tube was then sputter-coated with 120 nm of palladium at a constant pressure of 0.063 Torr. After coating, the platforms were placed in a covered dish and stored in a desiccator until used. After a new platform was placed in a furnace tube, the spectrometer was conditioned as normally practiced by the instrument when it is initially started.

Table 1. Furnace Program

temp (°C)	ramp time (s)	hold time (s)	purge gas flow rate (mL min^{-1})	Ar	Ar/CH_4
120	5	60	300		X
1300	1	65	300		X
20	1	15	300	X	
2650	0	5	0	X	
2700	1	5	300	X	

Typically, 40 μL of the standard and diluent was pipetted by the autosampler into the furnace and subjected to the furnace program. Concentrations of 5–100 ng/mL were used to establish the calibration curves. The Ar/CH_4 gas mixture was introduced into the furnace for the first two steps (Table 1). Subsequently, 100% Ar was restored to the furnace for the remainder of the analysis.

RESULTS AND DISCUSSION

Since many elements are sufficiently volatile to experience a mass loss during the pyrolysis step of the furnace program, chemical modification is an important tenant of the stabilized temperature platform concept. Due to silicon's nonvolatile (2355 °C bp) and ubiquitous nature, matrix modifiers are not recommended for most

Table 2. Comparison of Atomization Conditions for 20 ng/L Si Spiked Samples

atomization profile conditions	area[a,b] A-s	atomization profile conditions	area[a,b] A-s
Pd-CH_4	0.158 ± 0.009	Pd only	0.101 ± 0.016
CH_4 only	0.144 ± 0.006	neither	0.099 ± 0.011

[a] Average of five measurements. [b] ± 95% confidence interval.

applications. However, the myriad problems associated with the formation of oxides and carbides require some type of chemical modification for measurements of low silicon concentration. Since palladium has a well-established reputation as a universal matrix modifier, it was chosen for study. To offset the silicon contamination problem associated with the use of Pd solutions, the L'vov platform was coated with Pd.

Peak Shape and Intensity. Figure 1 provides an example of a silicon absorption peak under varying furnace conditions, while Table 2 compares peak areas under these conditions. The sharpest peak with the greatest peak is when both Pd-coated and Ar/CH_4 are employed. With only the gas mixture the peak is broader and the peak area decreases by about 10%. Using Pd-coated platforms alone produces relatively sharp peaks, but with a 35% diminished peak area. Using the standard procedure alone results in a low, broad peak with an area about that of Pd alone. Reproducibility obtained when using the Pd-coated platform and the Ar/CH_4 gas mixture was much improved over that obtained with the standard method or with Pd alone.

Higher analyte sensitivity results from the use of the gas mixture and the Pd-coated platforms. Presumably, the Pd promotes the deposition of the methane gas onto the platform and forms a Pd−CH_4 adsorption bond due to its affinity for H. Sturgeon et al. (1989) determined that this occurred with the preconcentration of metal hydrides onto the Pd-coated surface. Significant increases in absorbance values for Si could be explained by the formation of Si−Pd−H_2 intermetallic compounds. The formation of these intermetallic compounds could be the reason for silicon's reduced capability of forming oxides and carbides.

Analytical Lifetime of the Graphite Platform. Predictably, the analytical lifetime of the palladium-coated graphite platform was related to the amount of Pd sputter-coated onto the surface. A relative standard deviation (RSD) of 5% was normally achieved with this procedure. After 100 or so firings, the RSD began to increase significantly above 5%. Characteristic mass (defined as the mass of the analyte in picograms that will provide an integrated absorbance of 0.0044) was normally around 35 pg/0.0044 A-s, and it also increased significantly at the same time as the RSD started to increase. Thus, the life of the platform was found to be 100 or so firings as shown by these measures of sensitivity and precision.

Calibration Curves for Various Concentrations. Calibration curves were constructed for the concentration range of 5−100 ng/mL. A calibration curve run with Ar/CH_4 and Pd-coated platforms gave an average correlation coefficient of 0.9994 with a slope of 0.0055 and an intercept of 0.003. The detection limit, based on 20 blank measurements, was 1.1 ng/mL. For comparison, the standard curve with the standard conditions (traditional uncoated platform and argon gas only) had a correlation coefficient of 0.97432 and an RSD of over 10%.

Table 3. Determination of Si in Spiked Samples

sample	added spike (ng/mL of water)	silicon content[a,b] (ng/mL)
row[c] 0	unspiked	9 ± 0.0
row 5	5	13 ± 1.2
row 15	15	23 ± 0.0
row 20	20	30 ± 1.3
row 40	40	48 ± 1.0

[a] Average of five measurements. [b] ± 95% confidence interval. [c] Reverse osmosis water.

Analysis of Samples. Since National Institute of Standards and Technology (NIST) Standard Reference Material samples are not available at nanograms per gram Si levels, spiked samples were used as a measure of analytical accuracy of the method. A range of concentration values for the spiked samples was chosen to demonstrate the sensitivity and dynamic range of the technique. Table 3 presents the results from the analysis of the spiked samples. All determinations were the average of five replicates and show excellent agreement with calculated values.

Conclusion. A graphite L'vov platform sputter-coated with a 120 nm layer of Pd and the use of an alternate gas (95% Ar/5% CH_4) demonstrate significant improvement in silicon measurement by ETAAS. The use of this combination improved peak sharpness, precision, and calibration accuracy.

ACKNOWLEDGMENT

We acknowledge with appreciation the use of the sputter coater and the high vacuum provided by the Southern Weed Science Laboratory (SWSL), the technical assistance of Darion Gibson, and the expert advice provided by Mr. Rex N. Paul of the SWSL.

LITERATURE CITED

Boize, L.; Gudin, G.; Purdue, G. The influence of leaf surface roughness on the spreading of oil droplets. *Ann. Appl. Biol.* **1976**, *84*, 205−211.

Chambers, G. V.; Bulawa, M. C.; McWhorter, C. G.; Hanks, J. E. Use of surface relationship models to predict the spreading of nonaqueous droplets on johnsongrass. In *Pesticide Formulations and Application Systems*; Bode, L. E., Chasin, D. G., Eds.; American Society for Testing and Materials: Philadelphia, PA, 1993; Vol. 11, pp 218−246.

Frech, W.; Cedegren, A. Investigations of reactions involved in flameless AA procedures. Part 7, Theoretical and experimental study of factors influencing determination of Si. *Anal. Chim. Acta* **1980**, *113*, 227−235.

Gaskin, E. G.; Stevens, P. J. G. Antagonism of the foliar uptake of glyphosate into plants by organosilicone surfactant. Part 2: Effects of surfactant structure and glycerol addition. *Pestic. Sci.* **1993**, *38*, 193−200.

Mahmood,T. M.; Qiao, H.; Jackson, K. W. Physical behaviour of nickel and copper modifiers used in the determination of selenium by electrothermal atomic absorption spectrometry. *J. Anal. Spectrom.* **1995**, *10*, 43−47.

McWhorter, C. G.; Paul, R. N.; Barrentine, W. L. Morphology, development, and recrystallization of epicuticular waxes of johnsongrass (*Sorghum halepense*). *Weed Sci.* **1990**, *38*, 22−33.

McWhorter, C. G.; Paul, R. N.; Outzs, J. C. Bicellular trichomes of johnsongrass (*Sorghum halepense*) leaves: morphology, histology, and function. *Weed Sci.* **1995**, *43*, 201−*208.*

Muller-Vogt, G.; Wendl, W. Reaction kinetics in the determination of Si by graphite furnace AAS. *Anal. Chem.* **1981**, *39*, 651−653.

Nater, E. A.; Burau, R. G. Alkali metal fluoride matrix modifiers for the determination of trace levels of silicon by

graphite furnace atomic absorption spectrometry. *Anal. Chim. Acta* **1989**, *220*, 83–88.

Rademeyer, C. J.; Vermaak, I. Atomization mechanisms of silicon in a graphite furnace atomizer. *J. Anal. At. Spectrom.* **1992**, *7*, 347–351.

Schleisman, A. J. J.; Bollinger, D. Problems in the determination of silicon in ultrapure acids by GFAA. Presented at the Pittsburgh Conference, New Orleans, March 5–10, 1995; Abstract 235.

Sturgeon, R. E.; Willie, S. N.; Berman, S. S. Sequestration of volatile element hydrides by platinum group for graphite furnace atomic absorption. *Spectrochim. Acta, Part B* **1989**, *44*, 667.

Received for review November 18, 1996. Revised manuscript received March 11, 1997. Accepted March 11, 1997.[⊗] M.H., J.S., and M.S. acknowledge the support provided by the U.S. Department of Agriculture, ARS, under Research Contract Project 6402-21220-003005S.

JF9608736

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1997.