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Modification of electrothermal atomic absorption spectrometry for determination of arsenic in high salinity samples

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Abstract: The electrothermal atomic absorption spectrometry (ET-AAS) method was optimized for determination of the arsenic content in high salinity samples. The combination of palladium (1 g/l) modifier, graphite furnace temperature program and graphite tube modified with tungsten carbide significantly reduced the matrix interference in the sample with NaCl concentration of 10 g/l. Optimized temperature program ensured the reduction of the background absorbance about 95–100%. The modification of graphite furnace surface by tungsten carbides ensured the shift of background absorbance prior to the absorbance of the analyte and considerable extension lifetime of graphite tubes.

Key Words: arsenic, palladium modifier, tungsten carbide, ET-AAS, background correction

INTRODUCTION

Arsenic with mutagenic and carcinogenic effects on humans belongs among the highly toxic substances in the environment. Inorganic arsenic forms, such as arsenate (As^{V}) and arsenite (As^{III}), have higher toxicities than organic arsenic species. Human populations worldwide are primarily exposed to inorganic arsenic through the consumption of contaminated water (Cubadda et al. 2017). Determination of total arsenic content in aqueous samples is usually performed by electrothermal atomic absorption spectrometry. Arsenic determination by ET-AAS may be complicated by losses of the analyte during the pyrolysis stage and interferences caused by matrix (e.g., sea water, mineralized water) (Bermejo-Barrera et al. 1996, Bozsai et al. 1990, Welz et al. 1988).

The most, palladium nitrate or palladium-magnesium nitrate modifiers are used for determination of arsenic content in high salinity samples (Bermejo-Barrera et al. 1996, Welz et al. 1988). This modifiers cause stabilization of volatile analytes, including arsenic, to higher pyrolysis temperatures, and ensure the separation of the arsenic from the matrix during the pyrolysis phase without the loss of analyte. Reducing the background absorption can also be achieved by inserting a pre-atomization cool-down step into the graphite furnace temperature program (Bozsai et al. 1990, Cabon 2000, Pszonicki and Dudek 1999) or surface-modified graphite tubes (Kulik et al. 2009, Volynsky 1998).

The aim of this study was to optimize the ET-AAS method for arsenic determination in high salinity samples. The combination of palladium modifier, graphite furnace temperature program and graphite tube modified with tungsten carbide was tested and optimized for sensitive and precise arsenic determination.

MATERIAL AND METHODS

Instrumentation

Measurements were performed using graphite furnace atomic absorption spectrometer 280Z AA (Agilent Technologies, Santa Clara, CA, USA) with Zeeman background correction. Determination of arsenic was carried out under the conditions recommended by the manufacturer for As (193.7 nm) with a spectral bandwidth of 0.5 nm. Ultrasensitive hollow cathode lamp (Agilent Technologies, Santa Clara, CA, USA) was used as the radiation source of As (lamp current 10 mA). The ultrasonic bath Elmasonic P (Elma, Singen, Germany) was used for graphite furnace surface-modification.

Reagents

All solutions were prepared from analytical grade chemicals. Arsenic (III) standard solution with the concentration of 1000 ± 4 mg/l (Fluka, Czech Republic) was used for the preparation of calibration solutions (calibration range 0–100 µg/l). Palladium 10 g/l (Fluka, Czech Republic) was used for the preparation of 1% (v/v) Pd modifier and $Na_2WO_4 \cdot 2H_2O$ (Lachema, Czech Republic) was used for graphite furnace surface-modification. The 65% HNO_3 (Penta, Czech Republic) purified by sub-boiling distillation apparatus (Type BSB-939IR, Berghof, Eningen, Germany) and demineralized water produced by Millipore Milli Q system (Millipore, Bedford, MA, USA) were used for sample dilution.

Graphite furnace surface-modification

Pyrolytic graphite tubes were impregnated with aqueous solution Na_2WO_4 (50 g/l). Tubes were placed in the solution and soaked for 3 minutes in the ultrasonic bath under atmospheric pressure. Tubes were then carefully wiped and heated twice in the atomizer according to the graphite furnace temperature program (Table 2). The operation was repeated three times (Figure 1). Every day before the measurement starts, 10 µl of sodium tungsten solution (50 g/l) were dispensed onto the inner surface of the furnace and heated according to the graphite furnace temperature program (Table 2).

Figure 1 Scheme of graphite furnace surface-modification

Procedure

The standard arsenic solution (50 µg/l) in solution NaCl (10 g/l) was used for method optimization. The samples were acidified with 3% (v/v) HNO_3 before analysis. The palladium modifier (injection volume 10 µl) was pre-injected into graphite furnace before the sample injection (sampling volume 20 µl).

RESULTS AND DISCUSSION

Graphite furnace program optimization

Firstly, arsenic content in the sample with high concentration of NaCl (10 g/l) was measured under the graphite furnace temperature program recommended by the manufacturer of ET-AAS (Table 1). The palladium (1% v/v) was used as the modifier.

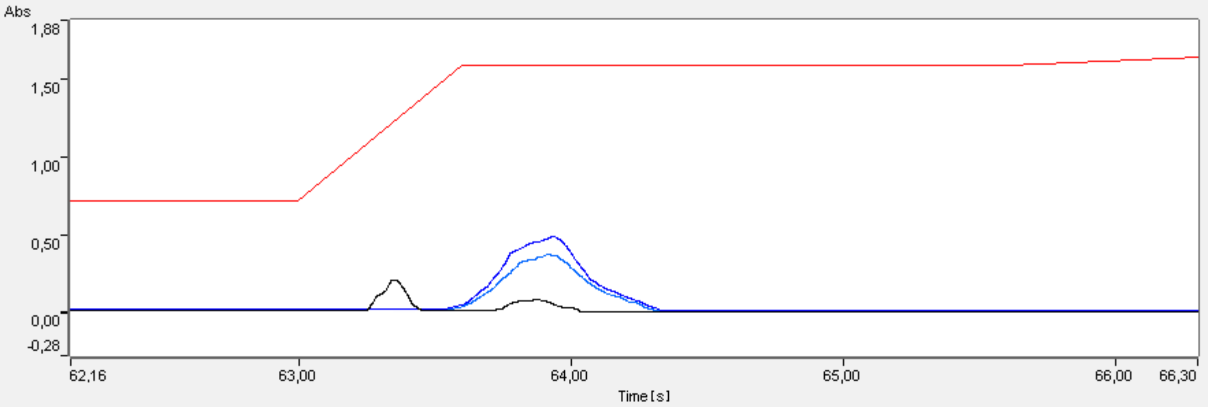
Table 1 Graphite furnace temperature program recommended by the manufacturer of ET-AAS

Step	1	2	3	4	5	6	7
Temperature, *°C*	85	95	120	1400	1400	2600	2800
Ramp time, *sec*	5	40	10	5		0.6	2
Hold time, *sec*				1	2	2	
Read						ON	
Argon flow, *l/min*	0.3	0.3	0.3	0.3	0	0	0.3

Legend: 1,2,3 – drying steps; 4,5 – pyrolysis steps; 6 – atomization step; 7 – cleaning step

High concentration of sodium chloride in the sample matrix generated high background absorbance which deformed the absorbance of analyte (Figure 2). When the temperature program recommended by the manufacturer was used for arsenic determination, the method recovery of arsenic in the sample with high salinity was only 50–70% with RSD = 17.8%. The limit of detection for As in solution NaCl (10 g/l) was 12.2 µg/l (sample volume 20 µl, 10 replicates).

Figure 2 The absorption signal of arsenic at temperature program stated in Table 1



Legend: Red line – temperature program; blue line – analyte absorbance; black line – background absorbance

To reduce the background absorption a cool-down step before atomization was incorporated into the graphite furnace temperature program (Table 2). Longer duration of drying step prevented boiling of the sample in the graphite tube.

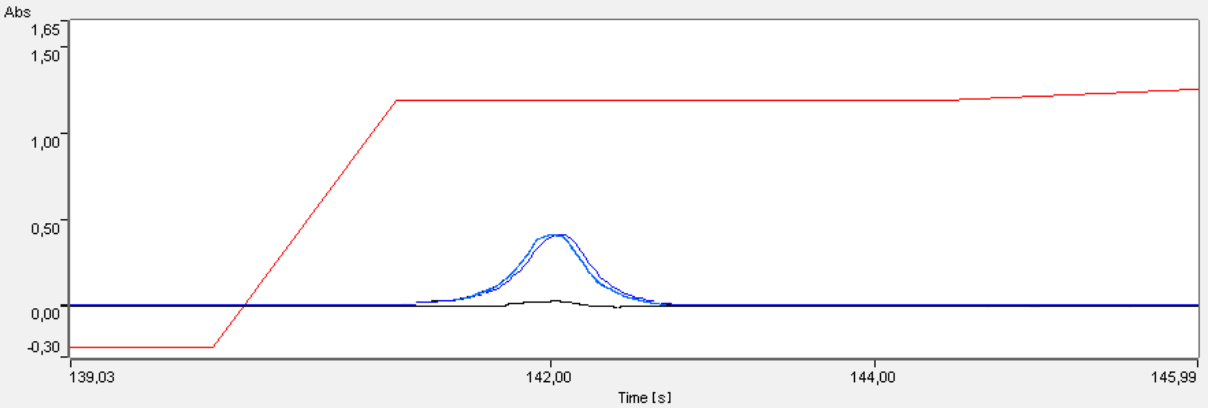
Table 2 Graphite furnace temperature program with pre-atomization cool-down step

Step	1	2	3	4	5	6	7
Temperature, *°C*	90	150	300	1300	130	2300	2650
Ramp time, *sec*	9	30	25	10	15	1	5
Hold time, *sec*		20		30	1	3	
Read						ON	
Argon flow, *l/min*	0.3	0.3	0.3	0.3	0.3	0	0.3

Legend: 1,2,3 – drying steps; 4 – pyrolysis step; 5 – cool-down step; 6 – atomization step; 7 – cleaning step

A cool-down step between the steps of pyrolysis and atomization ensured that the sample matrix effect was reduced, and the background absorption was lower about 95–100% (Figure 3). The RSD was decreased to less than 1%. The method recovery of arsenic with temperature program using cool-down step was 98–100%. Limit of detection for As in solution NaCl (10 g/l) was decreased to 1.1 µg/l (sample volume 20 µl, 10 replicates).

Figure 3 The absorption signal of arsenic at temperature program stated in Table 2 (with pre-atomization cool-down step)



Legend: Red line – temperature program; blue line – analyte absorbance; black line – background absorbance

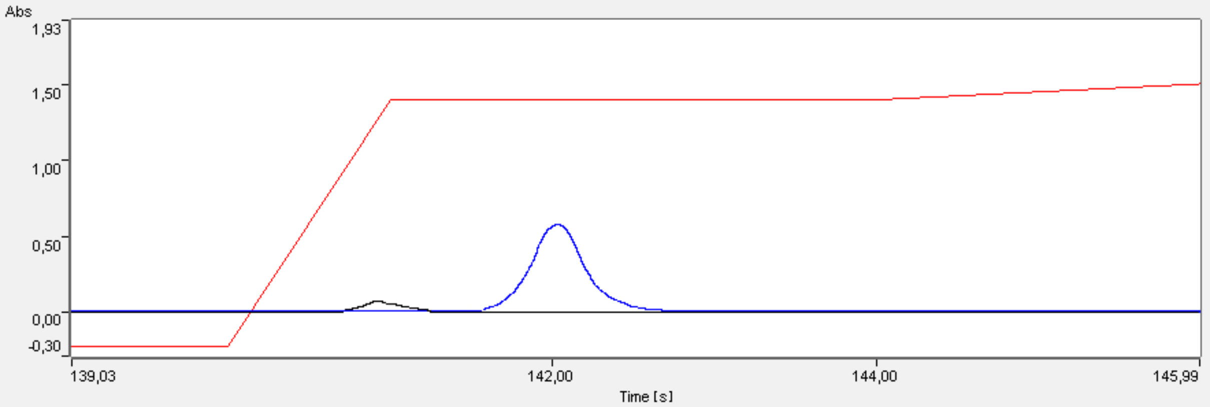
Bozsai et al. (1990) achieved similar results using palladium-magnesium nitrate modifier, pyrolysis temperature 1300 °C and the temperature drop after the pyrolysis step. It is assumed that high background absorbance is caused by Rayleigh scattering by larger salt particles in the cooler regions at the tube ends. When the pre-atomization cool-down step is incorporated into the graphite furnace temperature program, the tube is heated more uniformly and the effect of the cool tube ends is avoided almost completely (Bozsai et al. 1990).

Moreover, standard addition calibration method instead of matrix-free calibration was used to reduction matrix interferences. This step improved the performance of the methodology and made it independent of the knowledge of the NaCl concentration in the sample.

Graphite furnace surface-modification

Although we have achieved very good results of arsenic recovery through temperature program improvement, the lifetime of the graphite tube was reduced due to the aggressive composition of the sample matrix. The surface of the graphite tube was significantly damaged after about 50 firing cycles. For this reason, we have combined the cool-down step temperature program with the modification of graphite furnace surface by tungsten carbides.

Figure 4 The absorption signal of arsenic at temperature program stated in Table 2 (pre-atomization cool-down step) and at the modification of graphite furnace surface by tungsten carbides



Legend: Red line – temperature program; blue line – analyte absorbance; black line – background absorbance

The modification of graphite furnace surface by tungsten carbides led to the shift of the total background absorbance prior to the actual absorbance of the analyte. This prevents the distortion of the analyte absorbance (Figure 4). The lifetime of the graphite tube was significantly increased to 250 firing cycles.

CONCLUSION

The sensitive and precise method has been proposed and optimized for arsenic determination in samples containing high concentrations of chlorides. The interference effect of the sample matrix was reduced by the combination of palladium (1 g/l) modifier, graphite furnace temperature program with the cool-down pre-atomization step and graphite tube modified with tungsten carbides. The background absorbance was reduced about 95–100%. The new methodology allowed the determination of arsenic in solution NaCl (10 g/l) with the recovery of 98–100%. Limit of detection was decreased 11.3 times. Moreover, the lifetime of the graphite tube was increased five times.

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REFERENCES

Bermejo-Barrera, P. et al. 1996. Comparison of different chemical modifiers for the direct determination of arsenic in sea water by electrothermal atomic absorption spectrometry. Fresenius Journal of Analytical Chemistry, 355: 174–179.

Bozsai, G. et al. 1990. Determination of arsenic, cadmium, lead and selenium in highly mineralized waters by graphite-furnace atomic-absorption spectrometry. Talanta, 37(6): 554–553.

Cabon, J.Y. 2000. Effects of various salts on the determination of arsenic by graphite furnace atomic absorption spectrometry. Direct determination in seawater. Fresenius Journal of Analytical Chemistry, 367: 714–721.

Cubadda, F. et al. 2017. Human exposure to dietary inorganic arsenic and other arsenic species: State of knowledge, gaps and uncertainties. Science of the Total Environment, 579: 1228–1239.

Kulik, A.N. et al. 2009. Tungsten-assisted modification of graphite furnaces for an atomic absorption spectrometer. Journal of Applied Spectroscopy, 76(4): 564–569.

Pszonicki, L., Dudek, J. 1999. Modifier effects in the determination of arsenic, antimony and bismuth by electrothermal atomic absorption spectrometry. Journal of Analytical Atomic Spectrometry, 14: 1755–1760.

Volynsky, A.B. 1998. Graphite atomizers modified with high-melting carbides for electrothermal atomic absorption spectrometry. II. Practical aspects. Spectrochimica Acta Part B: Atomic Spectroscopy, 53(12): 1607–1644.

Welz, B. et al. 1988. Palladium nitrate – magnesium nitrate modifier for graphite furnace atomic absorption spectrometry. Part 2. Determination of arsenic, cadmium, copper, manganese, lead, antimony, selenium and thallium in water. Journal of Analytical Atomic Spectrometry, 3: 695–701.

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