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COLLOIDAL PALLADIUM MODIFIER: THEORY AND PRACTICAL APPLICATION FOR THE DETERMINATION OF ARSENIC, ANTIMONY AND LEAD IN A SPIKED SEA WATER BY ETAAS

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Abstract

Colloidal palladium is a prospective modifier for electrothermal atomic absorption spectrometry (ETAAS). Owing to high effectiveness of metallic palladium in the stabilization of volatile analyte compounds, colloidal palladium modifier is very robust in its action. In the presence of colloidal palladium, interference-free determinations of As, Sb and Pb are possible up to at least 450 μg of chloride ion or 40 μg of sulphate ion (as corresponding sodium salts) in the atomizer. Colloidal palladium was used for the direct determination of As, Sb and Pb in a spiked sea water sample (from Bosphorus channel near Istanbul) by means of the calibration graphs prepared with pure analyte solutions. The detection limits for As, Sb and Pb in a sea water matrix calculated according to 2σ criteria are 5.4 ng ml^{-1}, 3.6 ng ml^{-1} and 1.1 ng ml^{-1}, respectively (for sample volume 10 μl). In unspiked sea water, the contents of As, Sb and Pb were found to be below the detection limits. Recoveries of spiked analytes (25 ng ml^{-1} and 50 ng ml^{-1}) were in the region of 98-112% depending on the nature of analyte and the concentration of spike.

Keywords: electrothermal atomic absorption spectrometry; chemical modifiers; colloidal palladium; antimony; arsenic; lead; sea water.

1. Introduction

As is known, active forms of palladium modifier are elemental Pd, its oxide and intercalation compounds of palladium with graphite (see refs. in [1]). However, during analysis of complex samples palladium salts used as modifiers tend to be transformed to the corresponding chlorides [2]. Formation of palladium chlorides that cannot stabilize volatile analyte compounds during the pyrolysis stage seems to be the most widespread reason for low effectiveness of palladium modifiers sometimes reported.

Colloidal palladium has to be much more robust modifier because it 1) may interact with the analyte compounds already during drying; 2) quite inert not to interact with most matrices at moderate temperatures. Earlier investigations [3, 4] proved high effectiveness of colloidal palladium modifier for analysis of model solutions. In this work, the same modifier was used for the direct determination of As, Sb and Pb in a spiked sea water sample (from Bosphorus channel) by means of the calibration graphs prepared with pure analyte solutions.

2. Experimental

Reagents of “pro analysi” grade or higher purity (Merck) and stock standard solutions (Merck) were used. Before use, the original standard Sb and As solutions were diluted with 0.1 mol l^{-1} HCl. Lead standard solution was prepared in 0.1 mol l^{-1} HNO_3. Solutions of NaCl and Na_2SO_4

were prepared with doubly distilled water. Polyvinylpyrrolidone (PVP) K-90 (Mr ≈ 360 000) “for molecular biology” was purchased from Fluka. Polymer-stabilized colloidal palladium containing 3 mg ml^{-1} Pd was synthesized according to the modified procedure of Hirai and Toshima [5, 6].

Measurements were performed with a Jena Model EA 6 Vario atomic absorption spectrometer equipped with a D_2-lamp background corrector, as well as with an integrated side-heated graphite atomizer and an MPE 5 autosampler. Graphite tubes with a pyrolytic graphite coating and platforms made of a pyrolytic graphite were used throughout the work.

The total volume of the solution pipetted into the atomizer never exceeded 15 µl. Peak areas and peak heights were used for evaluation of atomic and background absorption, respectively. Each experiment was carried out with at least two replicates. As a rule, the reproducibility of the measurements was better than 10 %. Experimental conditions and instrumental parameters used are given in Table 1.

Table 1. Instrumental parameters and time/temperature programs of the electrothermal atomizer (temperature of the stage, °C/ramp rate, °C s^{-1}/hold time, s) used in the ETAAS measurements

	Analyte		
Parameter	Sb	As	Pb
λ, nm	217.6	193.7	217.0
Bandwidth, nm	0.2	0.5	0.2
Hollow cathode lamp	Beckman	Jena	Jena
Lamp current, mA	25	10	8
Characteristic mass in the presence of the modifier, pg	3.4	3.3	0.72
Drying (I)	90 °C/10 °C s^{-1}/5 s		
Drying (II)	120 °C/15 °C s^{-1}/20 s		
Pyrolysis temperature, ^{0}C	1000-1400	1100-1300	900-1200
Pyrolysis ramp rate, °C s^{-1}	100	100	100
Pyrolysis time, s	20∗ (50∗∗)	20∗ (50∗∗)	20∗ (50∗∗)
Atomization temperature, ^{0}C (gas stop)	2100-2200	2200-2400	1800-2200
Atomization ramp rate, °C s^{-1}	2000	2000	2000
Atomization time, s	4	4	5
Cleaning	2500 °C/1000 °C s^{-1}/2 s		

∗Pure solutions

∗∗In the presence of matrix

3. Results and discussion

Effectiveness of the modifiers depends greatly upon their mass and the time-temperature program of atomizer used. To demonstrate high potential of colloidal palladium modifier, we optimized only pyrolysis and atomization temperatures. Heating rate of the atomizer at the pyrolysis stage (100 °C s^{-1}) was taken from our previous works [3, 4]. Fixed hold time of the pyrolysis stage (50 s) was used. Palladium modifier mass was always 6 µg in the absence of matrix and 15 µg for all samples containing matrix, as in our previous work [4].

At first, we studied the effect of colloidal palladium for the determination of As, Sb and Pb in model solutions containing large amounts of NaCl and Na_2SO_4. As one can see from Figs. 1 and 2, under optimized conditions colloidal palladium modifier eliminates interferences effectively for all analytes studied. They may be determined quite precisely in the presence of at least 450 µg of chloride ion and 40 µg of sulphate ion with the use of pure aqueous solutions for calibration purposes. Relative standard deviations of analytical signals caused by variations of the matrix masses from zero up to their maximum tolerable amounts vary from 3.9% to 8.3%.

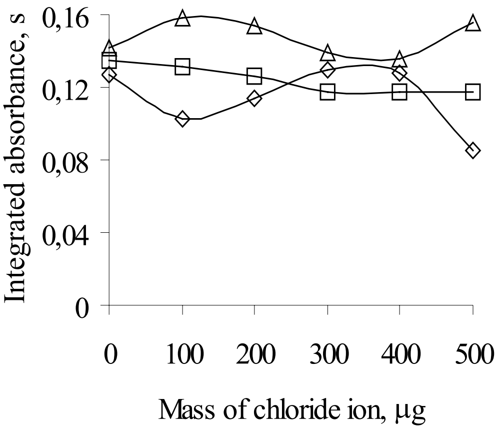

Fig. 1. Influence of sodium chloride on the determination of analytes in the presence of 15 µg of colloidal Pd modifier:
◊, 1 ng As (t_{pyr} = 1300 °C; t_{atom} = 2200 °C);
□, 1 ng Sb (t_{pyr} = 1200 °C; t_{atom} = 2100 °C);
Δ, 0.5 ng Pb (t_{pyr} = 1200 °C; t_{atom} = 1900 °C).

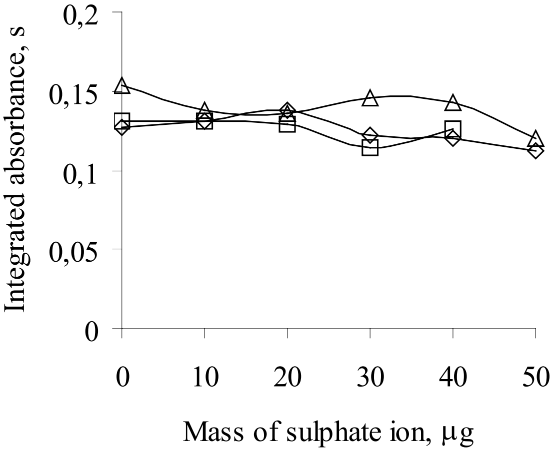

Fig. 2. Influence of sodium sulphate on the determination of analytes in the presence of 15 µg colloidal Pd modifier:
◊, 1 ng As (t_{pyr} = 1300 °C; t_{atom} = 2200 °C);
□, 1 ng Sb (t_{pyr} = 1000 °C; t_{atom} = 2100 °C);
Δ, 0.5 ng Pb (t_{pyr} = 1100 °C; t_{atom} = 2200 °C).

In most cases colloidal palladium modifier allows eliminating matrix interferences in systems studied to larger extent compared to a mixture of Pd and Mg nitrates [7, 8]. However, one must take into account that in both works [7, 8] the end-heated graphite atomizer (HGA-600) was used. As is known, atomizers of such a type are more susceptible to matrix interferences compared to side-heated atomizers (such as EA-6 used by us) (e. g., [9]). Therefore, the data obtained cannot be interpreted as a proof of superiority of colloidal palladium modifier over other palladium modifiers.

Sea water sample was taken from surface layer of Bosphorus channel near Istanbul (salinity 1.8%) and spiked with As, Sb and Pb. For all analytes studied, the temperature programs for the calibration graphs and for the sea water sample slightly differ, as well as amounts of the modifier applied (see above). However, as in the each case the determination conditions were optimum, recoveries of the spikes were very good. They varied in the region 98-112% with the relative standard deviation from 8% to 13% for 50 ng ml^{-1} of Sb and Pb, respectively (see Table 2).

Table 2. Determination of As, Sb and Pb in a spiked sea water sample (P=0.95, n=5)

Analyte	Concentration of spike, ng ml^{-1}	
	25	50
As (t_{pyr} = 1100 °C; t_{atom} = 2400 °C)	26±3	50±5
Sb (t_{pyr} = 1400 °C; t_{atom} = 2200 °C)	28±3	49±4
Pb (t_{pyr} = 900 °C; t_{atom} = 1800 °C)	27±3	52±7

The detection limits for As, Sb and Pb in a sea water matrix calculated according to 2σ criteria are 5.4 ng ml^{-1}, 3.6 ng ml^{-1} and 1.1 ng ml^{-1}, respectively (for sample volume 10 μl). In unspiked sea water, the contents of As, Sb and Pb were found to be below the detection limits of the method developed.

4. Conclusions

Colloidal palladium modifier proved its high effectiveness for analysis of complex samples. With minimum optimization of time-temperature program of the electrothermal atomizer and without optimization of amount of modifier, As, Sb and Pb spikes were successfully determined in a sea water matrix. For calculation of concentrations, calibration graphs of the basis of pure analyte solutions were applied. One may positively assume that colloidal palladium modifier is also effective for direct determination of many other analytes in real samples of various origin.

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