

Kinetic spectrophotometric determination of trace amounts of palladium by whole kinetic curve and a fixed time method using resazurine sulfide reaction

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Abstract

The univariate and multivariate calibration methods were applied for the determination of trace amounts of palladium based on the catalytic effect on the reaction between resazurine and sulfide. The decrease in absorbance of resazurine at 602 nm over a fixed time is proportional to the concentration of palladium over the range of 10.0–160.0 ng mL⁻¹. The calibration matrix for partial least squares (PLS) regression was designed with 14 samples. Orthogonal signal correction (OSC) is a preprocessing technique used for removing the information unrelated to the target variables based on constrained principal component analysis. OSC is a suitable preprocessing method for PLS calibration without loss of prediction ability using spectrophotometric method. The root mean square error of prediction (RMSEP) for palladium determination with fixed-time, PLS and OSC–PLS were 3.71, 2.84 and 0.68, respectively. This procedure allows the determination of palladium in synthetic and real samples with good reliability of the determination.

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1. Introduction

Interest in the development of analytical techniques for determination of the noble metals is growing as a result of their applications in chemical engineering, micromechanics and medicine. Palladium has been used in different areas of science and technology, including agents, brazing alloys, petroleum, electrical industries and catalytic chemical reactions [1–3]. The metal may enter the environment and interact with complexing materials, such as humic substances [4]. Palladium has no biological role, and all palladium compounds should be regarded as highly toxic and carcinogenic. Thus, because of its increasing use, on the one hand, and the toxicity of Pd(II) compounds to mammals, fish and higher plants, on the other hand [5], the determination of palladium is interesting in environmental analysis.

Kinetic methods have been widely used in this decade in catalytic and non-catalytic determination of various chemical

species, the different techniques and procedures associated with this type of method have been reviewed [6–12]. Several techniques such as complexometry [13], high-performance liquid chromatography [14], inductively coupled plasma [15], atomic absorption spectrometry [16,17], spectrophotometric [3,18], etc., have been used for determination of palladium in different samples. However, spectrophotometric methods have gained popularity for the determination of palladium due to their simplicity and low-operating costs.

The basic principle of the multivariate calibration is the simultaneous utilization of many independent variables, x_1, x_2, \dots, x_n , to quantify one or more dependent variables of interest, y . The partial least squares (PLS) regression analysis [19] is the most widely used method for this purpose, and it is based on the latent variable decomposition relating two blocks of variables, matrices x and y , which may contain spectral and concentration data, respectively. These matrices can be simultaneously decomposed into a sum of f latent variables, as follows:

$$X = TP^T + E = \sum t_f p'_f + E \quad (1)$$

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$$Y = UQ^T + F = \sum u_f q_f' + F \quad (2)$$

in which T and U are the score matrices for X and Y , respectively; P and Q are the loadings matrices for X and Y , respectively; E and F are the residual matrices. The two matrices are correlated by the scores T and U , for each latent variable, as follows:

$$u_f = b_f t_f \quad (3)$$

in which b_f is the regression coefficient for the f latent variable. The matrix Y can be calculated from u_f , as in Eq. (4), and the concentration of the new samples can be estimated from the new scores T^* , which are substituted in Eq. (4), leading to Eq. (5):

$$Y = TBQ^T + F \quad (4)$$

$$Y_{\text{new}} = T^*BQ^T \quad (5)$$

In this procedure, it is necessary to find the best number of latent variables, which is normally performed by using cross-validation, based on determination of minimum prediction error [19]. Several determinations based on the application of this method to spectrophotometric data have been reported by several studies [20–24].

Orthogonal signal correction (OSC) was introduced by Wold et al. [25] to remove systematic variation from the response matrix X that is unrelated, or orthogonal, to the property matrix Y . Therefore, one can be certain that important information regarding the analyte is retained. Since then, several groups [25–30] have published various OSC algorithms in an attempt to reduce model complexity by removing orthogonal components from the signal. Recently, application of orthogonal signal correction in UV–vis spectrophotometry for determination by partial least squares has been reported [31–33].

In this paper a simple, rapid, economical, selective and highly sensitive method has been presented for the spectrophotometric determination of trace amounts of palladium based on its catalytic effect on the resazurine sulfide reaction by application of partial least squares regression on the full kinetic curve and common fixed time method. The decrease in absorbance of the reagent, at $\lambda_{\text{max}} = 602$ nm, is proportional to the concentration of palladium. Various parameters have been evaluated, and the developed procedure has been successfully employed for determination of palladium in real samples.

2. Experimental

2.1. Apparatus and software

A Hewlett–Packard 8453 diode-array spectrophotometer controlled by a computer and equipped with a 1-cm path length quartz cell was used for spectra acquisition. Data acquisition at 602 nm was performed with UV-Visible ChemStation program (Agilent Technologies), running under Windows XP. Temperature was controlled by a thermostat.

The data were treated in a Pentium IV (CPU at 3.0 GHz and RAM 1 GB) personal computer using MATLAB software, version 6.5 (Math Works). OSC and PLS calculus were carried out in the PLS-Toolbox, version 2.0 (Eigenvectors Company).

2.2. Reagents

All chemicals were of analytical grade. Doubly distilled water was used for preparation of the solutions. Standard stock solution ($1000 \mu\text{g mL}^{-1}$) of palladium was prepared from commercial salt (nitrate) from Fluka. Standard working solutions were made by appropriate dilution daily as required. A stock resazurine (Fluka) solution (0.001 mol L^{-1}) was prepared by dissolving solid reagent in distilled water. Stock standard solution (0.5 mol L^{-1}) of sodium sulfide (Merck) was prepared. This solution was prepared fresh daily.

2.3. Recommended procedure

All the solutions and distilled water kept in thermostated water bath at 25°C for 20 min before starting the experiment. A 3.6 mL portion of resazurine was mixed with 1.2 mL portion of sodium sulfide and 0.5 mL portion of sodium hydroxide (1.0 mol L^{-1}) solution and diluted to 10 mL with water. Then 2 mL of this solution was transferred to the cell and finally proper amounts of standard palladium solution were injected to cell with μL syringe.

3. Results and discussion

3.1. Absorption spectra

It was found that the reaction between resazurine and sodium sulfide in basic media is very slow. The palladium could catalyze the reaction as trace amounts. However, when a trace amount of palladium is present, the reaction will proceed in a few minutes and the color of resazurine fades quickly. As can be seen from Fig. 1, the reaction rate increased in the presence of palladium and the absorbance decreased. As shown in Fig. 1, the absorption spectra reach their maximum in 602 nm both catalyzed reaction system. As a result, we selected 602 nm, as the measuring wavelength (Fig. 1a).

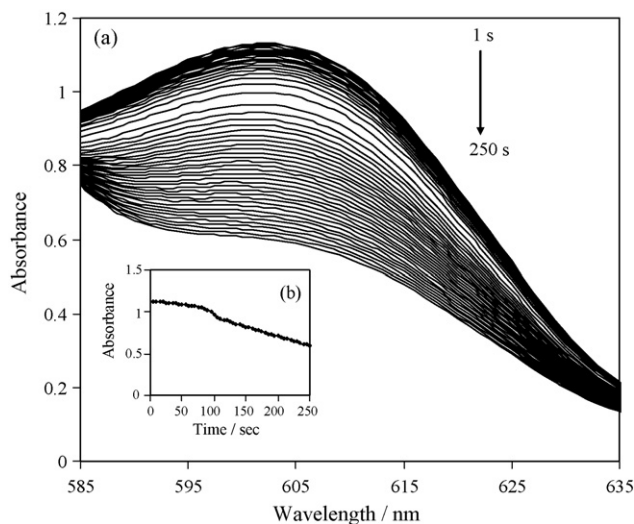


Fig. 1. (a) Illustration of a typical data set obtained in the monitoring of the catalytic effect of palladium in reaction of resazurine sodium sulfide in basic medium. (b) Absorbance-time plot at 602 nm (80 ng mL^{-1} of palladium).

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