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Simultaneous determination of antimony(III) and antimony(V) by UV–vis spectroscopy and partial least squares method (PLS)

M. Jesús Gómez González, Olga Domínguez Renedo, M. Julia Arcos Martínez *

Departamento de Química, Área de Química Analítica, Facultad de Ciencias, Universidad de Burgos, Plaza Misael Bañuelos s/n, E-09001 Burgos, Spain

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Abstract

This paper describes a procedure for the speciation of antimony by UV–vis spectroscopy using pyrogallol as complexing agent. A partial least squares (PLS) regression was performed to resolve highly overlapping spectrophotometric signals obtained from mixtures of Sb(III) and Sb(V). The relative error in absolute value was less than 5% when concentrations of several mixtures were calculated. The minimum concentration determined was 3.96×10^{-5} mol dm^{-3} and 3.98×10^{-5} mol dm^{-3} for Sb(V) and Sb(III), respectively. The analysis of the possible effect of the presence of foreign ions in the solution was performed and the procedure was successfully applied to the speciation of antimony in pharmaceutical preparations and aqueous samples.

Keywords: Speciation; Antimony; UV–vis spectroscopy; Multivariate calibration

1. Introduction

Antimony may be found in the environment as a result of various anthropogenic activities. Antimony-containing compounds are used in the manufacture of glass and ceramics as well as in fire retardants. Road traffic is also a significant source as it is used in brake linings and tyre vulcanization processes that require Sb-containing additives [1].

Unlike most other elements, antimony is more toxic than its organic compounds. The chemical form of its compounds considerably influences toxicity as does the oxidation state of antimony; Sb(III) being considerably more toxic and mobile than Sb(V). The availability of a sensitive and straightforward method would greatly facilitate the determination of both species.

Techniques such as atomic absorption spectrometry [2,3], plasma emission spectroscopy [4], neutron activation analysis [5] and chromatography techniques [6,7] have been used in the speciation of antimony. However, these techniques are neither sufficiently selective nor are they easily adapted to routine analyses. Atomic absorption spectrometry with hydride generation (HG-AAS) is the most widely used method [8–11]. This technique allows selective determination of Sb(III) to be successfully performed in the presence of Sb(V) [9], although it involves various long-drawn-out phases. In the first place, the Sb(III) content of the sample has to be determined, following which the total concentration of antimony has to be determined. Finally, the concentration of Sb(V) is arrived at by calculating the difference between the former and the latter values [8,10]. An alternative method of antimony speciation also using HG-AAS requires a somewhat lengthy process of extraction and separation of both species [11].

Spectrophotometry, due to its simplicity, is by far the most widespread method of analysis and is also used in antimony speciation. Abbaspour and Najafi [12] performed simultaneous spectrophotometric determination of Sb(III) and Sb(V) using pyrogallol red as a complexing agent, though they did not apply their method to the speciation of antimony in real samples.

The simultaneous determination of Sb(III) and Sb(V) in one single stage using UV–vis spectroscopy is difficult when both species are present in the medium because of

* Corresponding author. Tel.: +34 947 25 88 18; fax: +34 947 25 88 31.
E-mail address: jarcos@ubu.es (M.J.A. Martínez).

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highly overlapping signals, which prevent their calibration. Many processes propose solutions to the common problem of overlapping signals, of which the majority employ mathematical approaches [13–18]. Soft calibration methods such as "partial least squares" (PLS) [19–21], have made useful contributions to the resolution of overlapping signals and PLS is a proven method in the resolution of spectrophotometric [22] and electrochemical signals [23,24].

Leishmaniasis is an inflammatory disease, occurring in tropical regions, which affects 12 million people worldwide, and 1.5–2 million new cases of leishmaniasis are estimated to occur annually [25]. Treatment with antimonial drugs is the preferred method of combating this disease. The first antimonial drugs contained trivalent antimony, however, clinical benefits became associated with toxic effects and a second generation of antimonial drugs were developed based on pentavalent antimony. The quantities of Sb(V) and Sb(III) in these drugs are determined using spectrophotometry with bromopyrogallol red [26], which involves several stages. Firstly, the concentration of Sb(III) is directly determined. After subjecting the sample to a process of reduction, using iodide in a strong acid medium as a reducing agent, the total concentration of antimony is determined. Finally, the concentration of Sb(V) is calculated by subtraction. However, a technique for the speciation of antimony that does not require such long-drawn-out stages and lengthy pretreatment of samples would greatly improve upon existing methods.

The aim of our research is to simultaneously determine Sb(III) and Sb(V) in pharmaceutical preparations by UV–vis spectroscopy with pyrogallol as the complexing agent, without solvent extraction and by applying multivariate calibration methodology (PLSC).

2. Experimental

2.1. Materials and equipment

All solutions were prepared with deionised water from a Barnstead NANO Pure II system. Nitrogen (99.99%) was used to remove dissolved oxygen.

Stock standard solutions of Sb(V) were prepared by dissolving the appropriate amount of potassium hexahydroxyantimonate (V) (analytical-reagent grade, Sigma, Steinheim, Germany) in water. Sb(III) solutions were obtained by dissolving potassium antimony tartrate (III) (analytical-reagent grade, Sigma) in water.

Solutions of the chelating agent were prepared by dissolving the appropriate quantities of pyrogallol (analytical-reagent grade, Merck, Darmstadt, Germany) in water.

Britton–Robinson buffer pH 2 was used.

The procedure was used to analyse the pharmaceutical preparation Meglumina antimoniato (Glucantime®) 1.5 g/5 mL, Rhodia S.A.

Spectrophotometric measurements were taken using a Varian Cary 50 Conc. UV–vis spectrophotometer.

The pH of the solutions was measured with a Crison Model 2002 (Barcelona, Spain) pH meter.

Data analysis was performed using PARVUS [27] for the multivariate regression model.

3. Results and discussion

3.1. PLSC calibration

Fig. 1 shows the absorption spectra of the pyrogallol complexes with Sb(III) and Sb(V). The absorption peaks of these compounds continuously overlap each other, which rules out univariant calibration in the joint determination of both species, for which reason a multivariate regression using PLS was proposed for speciation.

With the aim testing the viability of a PLSC-calibration in the determination of mixtures of Sb(III) and Sb(V), 81 samples containing Sb(V) concentrations of between 1×10^{-6} mol dm^{-3} and 1×10^{-4} mol dm^{-3}, and Sb(III) concentrations of between 1×10^{-6} mol dm^{-3} and 1×10^{-4} mol dm^{-3}, were analyzed. The lower concentration of both species of antimony analyzed was 1×10^{-6} M, it was due to for lower concentrations no adequate analytical signal was obtained. In relation to the higher analyzed concentration, a value of 10^{-4} M was considered high enough since the aim of the method was the analysis of the trace levels of antimony.

The following procedure was used in the preparation and measurement of the different samples: 2 mL of a 1×10^{-2} mol dm^{-3} pyrogallol solution were added to a known volume of standard Sb(III) and Sb(V) solution made up to 100 mL with Britton–Robinson buffer (pH 2) in a volumetric flask.

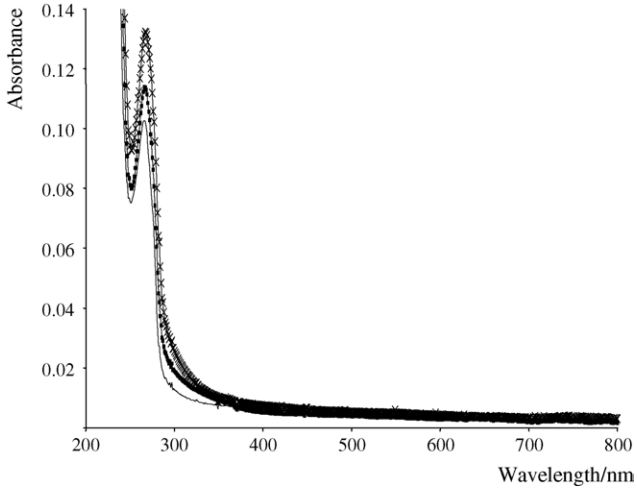

Fig. 1. UV–vis spectra of: (—), 10^{-4} mol dm^{-3} of Sb(III); (■), 10^{-4} mol dm^{-3} of Sb(V); (×), 5×10^{-5} mol dm^{-3} of Sb(III) and 5×10^{-5} of Sb(V). pH = 2 (Britton–Robinson); [pyrogallol] = 2×10^{-4} mol dm^{-3}.

Table 1
Variance explained in the blocks of predictors and response and cross-validate variance (C.V.) for the concentration of Sb(V) and Sb(III) by using the PLS model constructed with the original signal

Latent variables index	Sb(V)			Sb(III)		
	Explained variance of Y block (%)	C.V. Explained variance of Y block (%)	Variance of X block (%)	Explained variance of Y block (%)	C.V. Explained variance of Y block (%)	Variance of X block (%)
1	93.916	94.131	97.038	93.184	92.581	97.331
2	94.159	98.427	98.758	93.457	93.042	98.891
3	98.548	99.560[a]	99.091	93.703	96.653	98.972
4	98.664	99.521	99.117	94.207	98.044	99.157
5				99.139	98.110	99.209
6				99.242	98.376	99.232
7				99.289	98.920	99.272
8				99.403	99.007	99.300
9				99.745	99.065	99.341
10				99.796	99.086	99.369
11				99.896	99.104[a]	99.379
12				99.921	99.070	99.389

[a] Maximum cross-validate variance reached.

The solution was left for 30 min to allow sufficient time for a complex formation of Sb(V) and pyrogallol at room temperature. Finally, absorbance was measured from 200 nm up to 800 nm.

The PLSC model constructed with all 81 samples gave poor results, for which reason different PLSC models were constructed with separate subsets within the overall set of samples. The best results obtained, in the case of Sb(V), were for concentration zones ranging between 3.96×10^{-5} mol dm^{-3} and 9.94×10^{-5} mol dm^{-3} and, in the case of Sb(III), between 3.98×10^{-5} mol dm^{-3} and 9.90×10^{-5} mol dm^{-3}. All the spectra were digitalized, giving absorbance readings at 71 wavelengths between 220 nm and 290 nm for the determination of Sb(III) and at 101 wavelengths between 220 nm and 320 nm for the determination of Sb(V).

PLS is a widely used regression method in which information from the concentration values is used in the calculation of the so-called latent variables, which are linear combinations of the original variables. To maintain the maximum prediction ability of the model, it is convenient to optimize the predictive residual error sum-of-squares (PRESS) of the PLS models, constructed with the calibration data [22,28]; thus:

$$\mathrm{PRESS}(k) = \sum_{i=1}^{m} (c_i - \hat{c}_{k/i})^2$$

in which c_i is the concentration corresponding to the ith calibration sample (ith element of the vector c), and $\hat{c}_{k/i}$ is the concentration estimated by the PLS model with k latent variables calculated when the ith sample is removed. In practice, a more stable estimation is obtained if, instead of eliminating only one sample to calculate the concentration of k latent variables, the highest possible fraction of the samples is cancelled. The importance of full cross-validation [29], compared with partial cross-validation [30,31] has been shown. In other words, it is essential that neither the cancellation group nor an initial autoscaling of all the samples should intervene in the process of calculating the PLS model. If the data were autoscaled, the mean and variance of all the samples would intervene. In this work, the full cross-validation procedure-PLSC-is used instead of partial cross-validation.

Calculation of the PRESS involved was done with three cancellation groups by constructing three PLSC models for a number of latent variables, eliminating 9, 8 and 8, respectively, from the 25 absorption spectra [23,32].

Table 1 shows the results in percentages of explained variance and cross-validation variance as a function of the number of latent variables. It is clear that the inclusion of new latent variables causes the explained variance to rise; however, if the model includes an ith latent variable unrelated to the response, rather than continuing to increase, the cross-validate variance will decrease. The minimum PRESS is reached for the number of latent variables that give the maximum cross-validate variance.

In accordance with this criterion, 3 and 11 latent variables had to be taken for Sb(V) and Sb(III), respectively. In all cases, the cross-validate variance exceeded 99%.

The concentration found with this model for each antimony species was compared to the true value. Table 2 shows the values for true concentrations of Sb(V) and Sb(III), calculated with the PLSC model for the 25 calibration samples. The average relative absolute error obtained was 4.8% in the calibration of Sb(V) and 0.8% in the case of Sb(III).

In order to check the performance of the PLSC-calibration models, they were applied to a test set of four additional solutions, which differed from those upon which the model was built. At this stage, the figure of merit considered was accuracy, which includes precision and trueness (Table 3).

The accuracy of the predictions, or total error, was calculated as the mean square error of prediction (MSEP) and as a percentage, through the relative root mean square error of

Table 2
Concentrations calculated with PLSC model and relative errors in absolute obtained in the determination of the concentration of Sb(V) and Sb(III)

Sample	[Sb(V)] real (mol dm^{-3})	[Sb(III)] real (mol dm^{-3})	[Sb(V)] found (mol dm^{-3})	Relative absolute error (%)	[Sb(III)] found (mol dm^{-3})	Relative absolute error (%)
1	3.98×10^{-5}	4.97×10^{-5}	4.14×10^{-5}	4.02	4.90×10^{-5}	1.41
2	3.96×10^{-5}	8.92×10^{-5}	3.92×10^{-5}	1.01	8.95×10^{-5}	0.34
3	3.96×10^{-5}	9.90×10^{-5}	3.66×10^{-5}	7.58	9.90×10^{-5}	0.00
4	4.97×10^{-5}	5.96×10^{-5}	4.77×10^{-5}	4.02	6.00×10^{-5}	0.67
5	4.96×10^{-5}	7.94×10^{-5}	4.60×10^{-5}	7.26	7.92×10^{-5}	0.25
6	4.95×10^{-5}	8.92×10^{-5}	4.45×10^{-5}	10.10	9.05×10^{-5}	1.46
7	4.95×10^{-5}	9.90×10^{-5}	4.96×10^{-5}	0.20	9.79×10^{-5}	1.11
8	5.98×10^{-5}	3.98×10^{-5}	6.33×10^{-5}	5.85	4.06×10^{-5}	2.01
9	5.96×10^{-5}	6.95×10^{-5}	6.06×10^{-5}	1.68	6.87×10^{-5}	1.15
10	5.95×10^{-5}	7.94×10^{-5}	6.44×10^{-5}	8.24	7.92×10^{-5}	0.25
11	5.94×10^{-5}	9.90×10^{-5}	6.58×10^{-5}	10.77	9.90×10^{-5}	0.00
12	6.97×10^{-5}	3.98×10^{-5}	6.84×10^{-5}	1.87	4.05×10^{-5}	1.76
13	6.95×10^{-5}	6.95×10^{-5}	7.35×10^{-5}	5.76	6.92×10^{-5}	0.43
14	6.93×10^{-5}	9.90×10^{-5}	7.95×10^{-5}	14.72	9.89×10^{-5}	0.10
15	7.97×10^{-5}	3.98×10^{-5}	8.07×10^{-5}	1.25	3.94×10^{-5}	1.01
16	7.96×10^{-5}	4.97×10^{-5}	7.61×10^{-5}	4.40	4.96×10^{-5}	0.20
17	7.94×10^{-5}	7.94×10^{-5}	8.40×10^{-5}	5.79	8.06×10^{-5}	1.51
18	7.93×10^{-5}	8.92×10^{-5}	7.95×10^{-5}	0.25	9.07×10^{-5}	1.68
19	8.95×10^{-5}	4.97×10^{-5}	9.24×10^{-5}	3.24	4.95×10^{-5}	0.40
20	8.93×10^{-5}	7.94×10^{-5}	8.84×10^{-5}	1.01	7.93×10^{-5}	0.13
21	8.91×10^{-5}	9.90×10^{-5}	8.73×10^{-5}	2.02	9.81×10^{-5}	0.91
22	9.94×10^{-5}	5.96×10^{-5}	9.59×10^{-5}	3.52	6.01×10^{-5}	0.84
23	9.93×10^{-5}	6.95×10^{-5}	9.14×10^{-5}	7.96	6.94×10^{-5}	0.14
24	9.90×10^{-5}	9.90×10^{-5}	9.60×10^{-5}	3.03	9.92×10^{-5}	0.20
25	8.94×10^{-5}	6.95×10^{-5}	8.47×10^{-5}	5.26	6.80×10^{-5}	2.16

prediction (RRMSEP).

$$\mathrm{MSEP}(k) = \frac{\sum_{i=1}^{e}(\hat{c}_i(k) - c_i)^2}{e} \quad \text{and}$$

$$\mathrm{RRMSEP}(k) = \frac{100}{\bar{c}}\sqrt{\mathrm{MSEP}}$$

in which, c_i is the concentration corresponding to the ith evaluation sample, $\hat{c}_i(k)$ the concentration estimated by the PLS model with only k latent variables for the same sample, e the number of samples in the test set and $\bar{c}$ is the mean of the real concentrations.

Precision or variance in the prediction can be estimated by calculating the bias-corrected mean square error of prediction (BCMSEP),

$$\mathrm{BCMSEP}(k) = \frac{\sum_{i=1}^{e}(\hat{c}_i(k) - c_i)^2 - \frac{\left[\sum_{i=1}^{e}(\hat{c}_i(k) - c_i)\right]^2}{e}}{e-1}$$

and can be statistically compared to the precision of another method, or with the same method under different conditions, by an F-test of comparison of variances.

Trueness is verified by the absence of bias, which can be evaluated with the joint confidence interval test (JCIT) of the slope and the intercept, taking into account errors on both axes for the real concentrations and the concentrations predicted by the model.

Since the predictions were unbiased at the usual 95% significance level ($F_{0.05,2,2} = 19$), while the prediction errors in terms of the RRMSEP were 3.61% for Sb(V) and 3.32% for Sb(III), it may be said that the proposed procedure is suitable for the joint calibration of both antimony species.

3.2. Interferences

Analysis of the possible effect of the presence of foreign ions in the solution was performed. Of all the metallic

Table 3
Concentration and prediction values obtained from the PLSC model in the determination of Sb(V) and Sb(III) in the four test samples

Test	[Sb(III)] true (mol dm^{-3})	[Sb(III)] found (mol dm^{-3})	[Sb(V)] true (mol dm^{-3})	[Sb(V)] found (mol dm^{-3})
t1	8.92×10^{-5}	9.33×10^{-5}	5.95×10^{-5}	6.11×10^{-5}
t2	6.95×10^{-5}	7.21×10^{-5}	7.94×10^{-5}	8.23×10^{-5}
t3	5.96×10^{-5}	6.11×10^{-5}	8.95×10^{-5}	9.11×10^{-5}
t4	8.92×10^{-5}	8.87×10^{-5}	8.92×10^{-5}	9.36×10^{-5}
MSEP	6.52×10^{-12}		8.22×10^{-12}	
RRMSEP	3.32		3.61	
BCMSEP	3.75×10^{-12}		1.78×10^{-12}	
JCIT (F_{cal})	1.33		8.07	

Table 4
Concentrations added and predictions values obtained with PLSC model in the simultaneous determination of Sb(III) and Sb(V) in spiked tap water samples

Sample	[Sb(III)] added (mol dm^{-3})	[Sb(III)] found (mol dm^{-3})	Recovery (%)	[Sb(V)] added (mol dm^{-3})	[Sb(V)] found (mol dm^{-3})	Recovery (%)
1	2.00×10^{-6}	$2.0 \times 10^{-6} \pm 1 \times 10^{-7}$	99.50	2.00×10^{-6}	$2.0 \times 10^{-6} \pm 1 \times 10^{-7}$	98.50
2	2.00×10^{-6}	$2.03 \times 10^{-6} \pm 9 \times 10^{-8}$	101.50	1.00×10^{-5}	$9.9 \times 10^{-6} \pm 1 \times 10^{-7}$	99.30
3	1.00×10^{-5}	$1.05 \times 10^{-5} \pm 5 \times 10^{-7}$	105.00	2.00×10^{-6}	$1.96 \times 10^{-6} \pm 9 \times 10^{-8}$	98.00

ions analysed – As(III), As(V), Cd(II), Cu(II), Fe(II), Fe(III), Ni(II), Pb(II) and Zn(II) – only Fe(II) and Ni(II), at concentrations higher than 10^{-3} mol dm^{-3}, and Fe(III), at concentrations higher than 10^{-4} mol dm^{-3}, were found to have an effect by giving absorption peaks in the same zone of wavelengths.

3.3. Analytical application

The PLSC model constructed in Section 3.1 was applied to the determination of both species of antimony in a commercial sample of Glucantime®, obtaining concentrations of $5.6 \times 10^{-2} \pm 0.23 \times 10^{-2}$ mol dm^{-3} and $6.40 \times 10^{-1} \pm 0.31 \times 10^{-1}$ mol dm^{-3} ($n = 3$, $\alpha = 0.05$) for Sb(III) and Sb(V), respectively. Good agreement was obtained between the concentrations found and the value of total Sb concentration as supplied by the manufacturer ($6.98 \times 10^{-1} \pm 0.35 \times 10^{-1}$ mol dm^{-3}). These results were also checked using ICP-MS as a reference technique obtaining $6.90 \times 10^{-1} \pm 0.46 \times 10^{-1}$ mol dm^{-3} ($n = 3$, $\alpha = 0.05$) for total antimony concentration.

The PLSC model constructed in Section 3.1 was also applied to the determination of both species of antimony in spiked tap water samples. Good agreement was obtained between the concentration added and the value obtained by the developed method as can be seen in Table 4.

4. Conclusions

PLS regression can be successfully applied to the speciation of antimony by UV–vis spectrophotometry using pyrogallol as a complexing agent. This rapid and relatively inexpensive method greatly facilitates the simultaneous determination of antimony species allowing Sb(III) and Sb(V) to be jointly determined in pharmaceutical preparations and water samples without lengthy pre-treatment phases.

The proposed method in this work offers an interesting alternative for antimony speciation using simple and easily available instrumentation even in the presence of high concentrations of other metals.

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