Simultaneous Kinetic Spectrophotometric Determination of Sulfite and Sulfide Using Partial Least Squares (PLS) Regression

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The partial least squares (PLS-1) calibration model based on spectrophotometric measurement, for the simultaneous determination of sulfite and sulfide is described. This method is based on the difference between the rate of the reaction of sulfide and sulfite with Malachite Green in pH 7.0 buffer solution and at 25 °C. The absorption kinetic profiles of the solutions were monitored by measuring the decrease in the absorbance of Malachite Green at 617 nm in the time range 10-180 s after initiation of the reactions with 2 s intervals. The experimental calibration matrix for partial least squares (PLS-1) calibration was designed with 24 samples. The cross-validation method was used for selecting the number of factors. The results showed that simultaneous determination could be performed in the range 0.030-1.5 and 0.030-1.2 μg mL^{-1} for sulfite and sulfide, respectively. The proposed method was successfully applied to simultaneous determination of sulfite and sulfide in water samples and whole human blood.

Key Words : Partial least squares (PLS), Sulfite, Sulfide, Spectrophotometric determination, Kinetic methods

Introduction

Interest in UV-Vis spectrophotometric methods has increased and been renewed through the use of signal processing and multivariate calibration,[1] partial least squares (PLS) regression[2,3] and artificial neural network (ANN).[4]

Multivariate calibration methods have an increased importance in multicomponent analysis, specially using PLS method with decomposition into latent variables.[5] The partial least squares (PLS) regression was successfully used in spectrophotometry[6-8] and near-infrared spectrometry.[9] Multicomponent kinetic determinations when associated with different chemometrics methods such as PLS and ANN can resolve multicomponent kinetic systems by using differences of behavior with respect to a common reagent[10-12] without requiring prior separation.

PLS calibration of a multicomponent system can be performed in two different ways, PLS1 and PLS2. The use of PLS2 has a few advantages. Firstly there is one common set of PLS factors for all analytes. This simplifies the procedure and interpretation and enables a simultaneous graphical inspection. Secondly, when the analyte concentrations are strongly correlated one may expect that the PLS2 model is more robust than separate PLS1 models. Finally, when the number of analytes is large the development of a single PLS2 model is done much quicker than development of many separate PLS1 models. Practical experience, however, indicates that PLS1 calibration usually performs equally well or better in terms of predictive accuracy. Thus, when the ultimate requirement of the calibration study is to enable the best possible prediction, a separate PLS1 regression for each analyte is advised. In the present work PLS1 models were used for determination of analytes.[13]

Sulfite is widely used as additive in food and beverages to prevent oxidation and bacterial growth and to control enzymatic reactions during production and storage. Sulfite is also known to present some cytotoxic, mutagenic and antinutritional effects.[14] In particularly, it interacts with some vitamins, i.e. pyridoxal, nicotinamide, thiamine, folic acid, reducing the nutritional quality of treated food.[15]

Sulfide is formed in waste water by action of anaerobic bacteria on organic matter. Reduced sulfur compounds, such as hydrogen sulfide are found in natural and waste waters. From the environmental point of view, hydrogen sulfide is one of the most important parameters to monitor in water matrices due to its high toxicity for aquatic organisms. Also, hydrogen sulfide controls the bioavailability of heavy metals in anoxic environments due to the low solubility of sulfide salts.[16]

The determination of sulfite and sulfide in biological and industrial samples is important. Different methods have been reported for determination of sulfite or sulfide. These include kinetic spectrophotometric methods,[17-20] chromatography[21,22] and electrochemical methods.[23-25] Ghasemi and Mohammadi applied univariate and multivariate calibration method for the determination of sulfite[26] and sulfide[27] based on their addition reaction with new fuchsin.

Several methods have been reported for simultaneous determination of sulfite and sulfide. These include, gas phase molecular absorption spectrometry,[28] chromatographic separation[29] and fluorometric flow-injection.[30] Recently ANNs were employed for the simultaneous determination of sulfite and sulfide.[31] A simultaneous kinetic resolution of binary mixtures of cyanide, sulfide, and sulfite by reaction with 5,5-dithiobis(2-nitrobenzoic acid) (DTNB) in aqueous cetyltrimethylammonium bromide (CTAB) micelles was developed.[32]

In this paper, we describe a rapid, simple, precise and accurate method for the simultaneous determination of

sulfite and sulfide using the partial least squares (PLS-1) regression. The method is based on the difference between the rate of their reactions with Malachite Green in pH 7.0 buffer solution and at 25 °C. The absorption kinetic profiles of the solutions were monitored by measuring the decrease in the absorbance of Malachite Green at 617 nm in the time range 10-180 s after initiation of the reaction with 2 s intervals.

Experimental Section

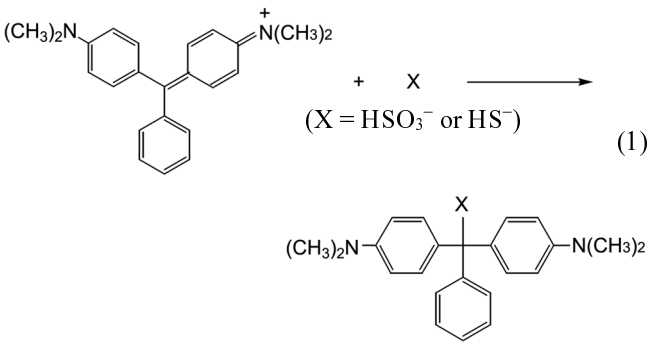
Apparatus. A Pharmacia Model LKB3 UV-visible Ultraspect(III) single beam spectrophotometer that connected to a Pentium II computer with 1-cm quartz cells was used for recording the kinetic profiles. A Jenway C_{15} pH-meter was used to adjust the pH of the buffered solutions. The computations were made with a Pentium 4 computer. The PLS calculations were performed with the PLS_Toolbox for MATLAB version 3.5.

Reagents. Triply distilled water and analytical reagent grade chemicals were used. A 1000 μg mL^{-1} standard solutions of sulfide and sulfite were prepared daily by dissolving 0.7500 g of $Na_2S{\cdot}9H_2O$ (Merck) and 0.1574 g of Na_2SO_3 (Merck) in water and diluting to the mark in a 100 mL volumetric flask. These solutions were standardized by iodometric titration.[25] Working solutions were prepared by diluting the standard solutions with water. A 2.20×10^{-4} M Malachite Green solution was prepared by dissolving 0.1023 g of Malachite Green (Merck) in water and diluting to 1000 mL with water. A 0.1 M phosphate buffer solution of pH 7.0 was prepared and its pH was checked by the pH meter.

Procedure. All the solutions were kept in a thermostated water bath at 25 ± 0.1 °C before beginning the reactions.

A 30 mL of 2.20×10^{-4} M Malachite Green and 30 mL phosphate buffer solution of pH 7.0 were added into a 100 mL volumetric flask and the solution was diluted to the mark with water. This solution was prepared daily. Then 1 mL of this solution was added into a 1-cm quartz cell containing 2 mL of sulfite and/or sulfide solution. The absorption kinetic profiles of the solutions contain of sulfite and sulfide with different concentrations were recorded at 617 nm in the time range 10-180 s with 2 s intervals after initiation of the reaction.

Results and Discussion



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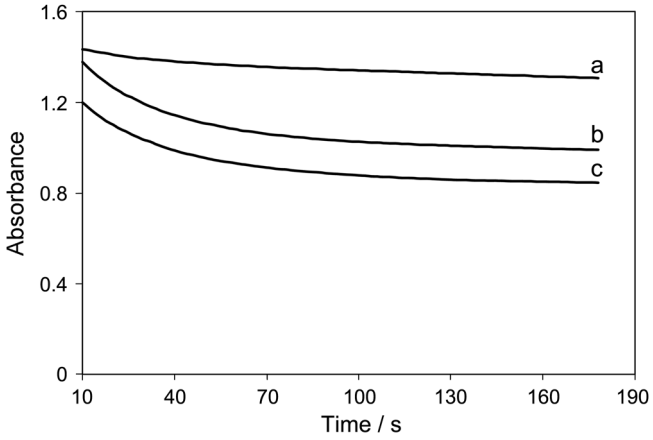

Figure 1. Kinetic profiles for Malachite Green in the reaction with (a) sulfite, (b) sulfide and (c) their mixture. Conditions: sulfite, 0.20 μg mL^{-1}; sulfide, 0.20 μg mL^{-1}; Malachite Green, 22 μM; pH = 7.0 and t = 25 °C.

Preliminary Investigations. In phosphate buffer solution of pH 7.0 and at 25 °C, sulfite and sulfide react with Malachite Green and decolorize it.

The reactions can be monitored spectrophotometrically by measuring the decrease in the absorbance of the solution at 617 nm.

It was observed that under the similar conditions the rate of the reaction of hydrogen sulfite and hydrogen sulfide with Malachite Green are different (see Figure 1). Therefore, the system seems to be appropriate for simultaneous determination of sulfite and sulfide by spectrophotometric method using the partial least squares (PLS) calibration.

Effect of Variables. The effect of pH on the rate of the reactions of a mixture of sulfite and sulfide was studied in the range 4-12. The results are shown in Figure 2. As Figure 2 shows, the absorbance change increased by increasing pH up to 7.0 and decrease at higher pHs. Therefore, pH 7.0 was selected as the optimum pH.

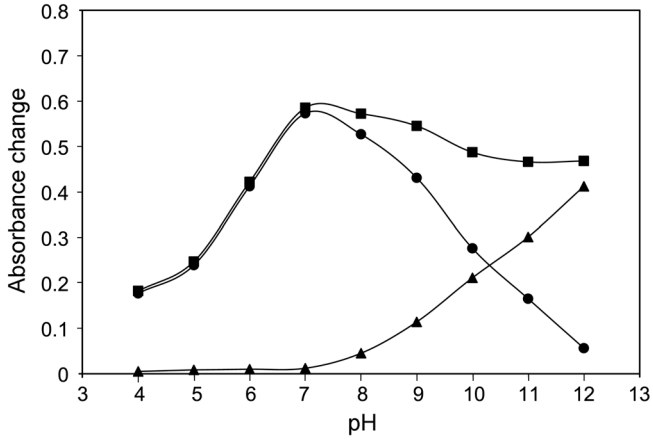

Figure 2. Effect of pH on the rate of the reaction of (■) sulfite and sulfide with Malachite Green, (▲) blank reaction and (●) their difference. Conditions: sulfite, 0.20 μg mL^{-1}; sulfide, 0.20 μg mL^{-1}; Malachite Green, 22 μM and t = 25 °C.

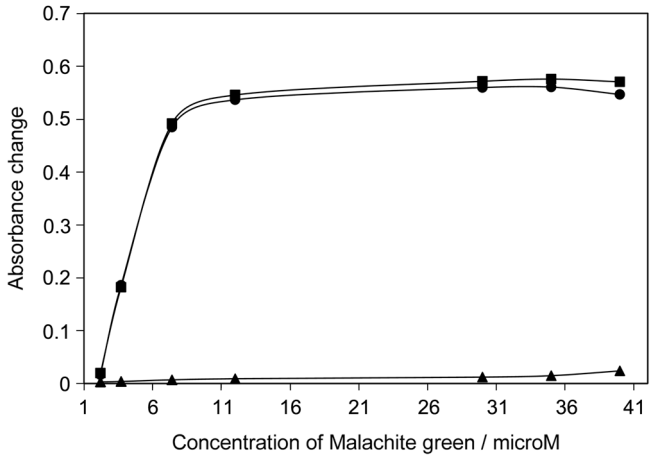

Figure 3. Effect of Malachite Green concentration on the rate of the reaction of (■) sulfite and sulfide with Malachite Green, (▲) blank reaction and (●) their difference. Conditions: sulfite, 0.20 μg mL^{-1}; sulfide, 0.20 μg mL^{-1}; pH = 7.0 and t = 25 °C.

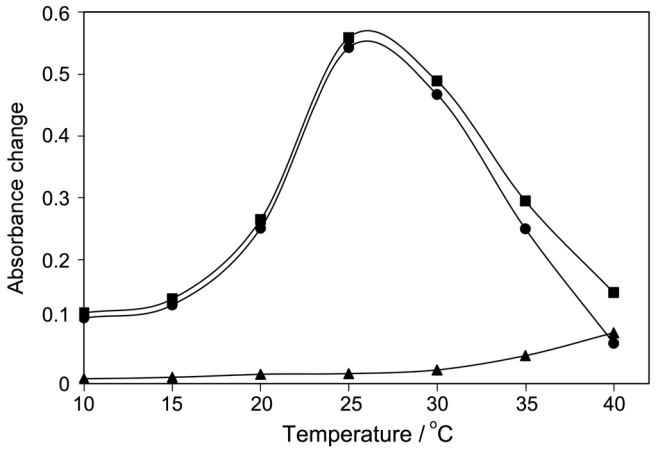

Figure 4. Effect of temperature on the rate of the reaction of (■) sulfite and sulfide with Malachite Green, (▲) blank reaction and (●) their difference. Conditions: sulfite, 0.20 μg mL^{-1}; sulfide, 0.20 μg mL^{-1}; Malachite Green, μM and pH = 7.0.

The effect of Malachite Green concentration on the rate of the reactions of a mixture of sulfite and sulfide was studied in the range 2.2-40 μM. The results (Figure 3) show that the absorbance change increased by increasing concentration of Malachite Green up to 12 μM and remained constant at higher concentrations. As Therefore, a concentration of 22 μM of Malachite Green was selected as the optimum concentration.

The effect of temperature on the rate of reaction of mixture of sulfite and sulfide was studied in the range 10-40 °C. As Figure 4 shows, the absorbance change increased by increasing temperature up to 25 °C and decrease at higher temperatures. Therefore, a temperature of 25 °C was selected as the optimum temperature.

Table 2. Concentration data for the different mixtures used in the calibration set and prediction set for the determination of sulfite and sulfide

Calibration set/μg mL^{-1}		Prediction set/μg mL^{-1}	
Sulfite	Sulfide	Sulfite	Sulfide
0.30	0.0	0.90	0.0
0.60	0.0	0.30	0.24
1.2	0.0	1.5	0.24
1.5	0.0	1.2	0.48
0.0	0.24	0.60	0.48
0.30	0.24	0.60	0.72
0.90	0.24	0.0	0.96
1.2	0.24	0.90	0.96
0.0	0.48	0.30	1.2
0.30	0.48		
0.60	0.48		
0.90	0.48		
1.5	0.48		
0.0	0.72		
0.30	0.72		
0.90	0.72		
1.2	0.72		
0.30	0.96		
0.60	0.96		
1.2	0.96		
0.0	1.2		
0.60	1.2		
0.90	1.2		
1.5	1.2		

Univariate Calibration. Under the optimum conditions calibration graphs for sulfide and sulfite were constructed by plotting absorbance change values during 10-180 s after initiation of the reactions as a function of the analyte concentration. The calibration graphs were linear in the range of 0.03-1.50 and 0.03-1.20 μg mL^{-1} for sulfite and sulfide, respectively. The results are shown in Table 1.

Multivariate Calibration and Prediction Data Set. Multivariate calibration consists of the establishment of a relationship between matrices of chemical data. The methods are based on a first calibration step in which a mathematical model is built using a chemical data set (e.g. absorbance values) and a concentration matrix data set. The calibration is followed by a prediction step in which this model is used to estimate unknown concentrations of a mixture from its kinetic profile.

In particular, PCR and PLS techniques are called "factor methods" because transform the high number of original variables in to a smaller number of orthogonal variables called "factors" or "principal components", which are linear

Table 1. Characteristics of calibration graphs for the determination of sulfite and sulfide

Analyte	Slope/mL μg^{-1}	Intercept	Correlation coefficient	Linear range/μg mL^{-1}	Limit of Detection/μg mL^{-1}
Sulfite	0.6628	0.0526	0.9998	0.030-1.5	0.018
Sulfide	0.9206	0.0837	0.9999	0.030-1.2	0.013

combinations of the original variables. The first factors contain useful information, whereas the last ones represent the noise, which has to be discarded and not considered in the modeling.

Experimental design of the calibration set multivariate calibration methods such as PCR and PLS require a suitable experimental design of defining the calibration set. The calibration procedure in complete experimental design was selected with six concentration levels for both sulfite and sulfide. A synthetic set of 33 solutions of mixtures of sulfite and sulfide were prepared (Table 2). From the series, 24 solutions were chosen for the calibration set and 9 solutions were used as prediction solutions.

Procedure for Selecting the Optimal Number of Factors. The selection of the optimal number of factors (latent variables) used to build PLS models for represents a decisive step to improve the prediction power of the methods. A full cross-validation, also called leave one-out cross-validation, was employed towards this aim. It consists of removing one sample at a time from the calibration step and performing the calibration with all other samples. The concentration of the sample removed is then predicted with the obtained model. This step is in turn repeated for each sample considered. The procedure can be repeated after fixing a different number of factors. The prediction error was calculated for each ion for the prediction set, which are the samples not participating in the construction of the model. This error was expressed as the prediction residual error sum of squares (PRESS). PRESS was calculated for the first variable, which built the PLS-1 modeling in the calibration step, then, another latent variable was added for the model building and the PRESS was calculated again. This process was repeated for one to 9 latent variables, which were used in the PLS-1 modeling. This procedure was repeated for each element. Figure 5 shows the plot of PRESS against the number of factors for each individual component. One reasonable choice for the optimum number of factor would be the number which yield the minimum PRESS. The F-statistical test was used to determine the significance of PRESS values greater than the minimum. The optimal number of factors for sulfide and sulfite was obtained 3. The results obtained by applying PLS1 algorithm to the prediction set are given in Table 3.

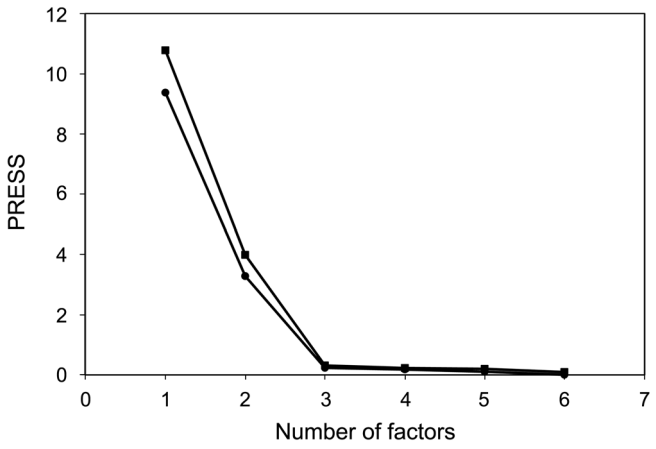

Figure 5. Plot of PRESS against the number of factors for (■) sulfite and (▼) sulfide.

Table 3. Composition of synthetic samples, their predictions by PLS-1 model and statistical parameters for system

Composition ($\mu g\ mL^{-1}$)		Prediction ($\mu g\ mL^{-1}$)		Recovery (%)	
Sulfide	Sulfite	Sulfide	Sulfite	Sulfide	Sulfite
0	0.9	0.04	0.9102	–	101.13
0.24	0.3	0.2395	0.3217	99.79	107.23
0.24	1.5	0.2415	1.4099	100.63	93.99
0.48	1.2	0.5057	1.1025	105.35	91.875
0.48	0.6	0.4893	0.6220	101.93	104.33
0.72	0.6	0.7321	0.6499	101.68	108.31
0.96	0	0.9655	0.058	100.57	–
0.96	0.9	0.9988	0.868	104.04	96.44
1.2	0.3	1.1035	0.33	91.958	111.3
Mean recovery				100.74	101.825

As Figures 2-4 show the change in absorbance strongly depends on pH, Malachite Green concentration and temperature. Therefore they are most effective factors in this method.

Statistical Parameters. The statistical treatment of this study is basically the same as that of Ghasemi and Mohammadi.[27] For the optimized model four parameters were selected, as some type of figures of merite, to evaluate the prediction ability of the model for determination of sulfide and sulfite in the prediction set. The root mean square difference (RMSD), which is an indication of the average error in the analysis, for each component:

$$\mathrm{RMSD} = [1/n\textstyle\sum_{j=1}^{N}(\hat{C} - C_j)]^{1/2} \quad (2)$$

The other parameter was relative error of prediction (REP) that shows the predictive ability of each component:

$$\mathrm{REP}\ (\%) = 100/C[1/n\textstyle\sum_{j=1}^{N}(\hat{C} - C_j)^2]^{1/2} \quad (3)$$

The prediction error of a single component in the mixture was calculated as the relative standard error (R.S.E) of the prediction concentration:[6,34]

$$\mathrm{R.S.E.}\ (\%) = [\textstyle\sum_{j=1}^{N}(\hat{C} - C_j)^2 / \sum_{j=1}^{N}(\hat{C} - C_j)^2]^{1/2} \times 100 \quad (4)$$

The total prediction error of N samples is calculated as follows:

$$\mathrm{R.S.E.}_t\ (\%) = [\textstyle\sum_{i=1}^{M}\sum_{j=1}^{N}(\hat{C}_{ij} - C_{ij})^2 / \sum_{i=1}^{M}\sum_{j=1}^{N}(C_{ij})^2]^{1/2} \times 100 \quad (5)$$

where N is the number of samples, C_j and $\hat{C}_j$ are the concentration of the component in the jth mixture and the

Table 4. Statistical parameters of the optimized matrix using the PLS-1 model

Anion	NPC[a]	RMSD	REP (%)	R.S.E.*single*	R.S.E.*total*
S^{2-}	3	0.0385	6.56	4.47	5.75
SO_3^{2-}	3	0.05422	7.7	6.5	5.75

[a]Number of principle components.

Table 5. Tolerance limits of diverse ions on the determination of a mixture of 0.50 μg mL^{-1} each of sulfite and sulfide

Ions	Tolerace limit/μg mL^{-1}
Cl^-, NO_2^-, NO_3^-, CO_3^{2-}, HCO_3^- ClO_3^-, SO_4^{2-}, $S_2O_8^{2-}$, F^-, PO_4^{3-} , Br^-, BrO_3^-, I^-, ClO_4^-, SCN^-, CH_3COO^-, Pb^{2+}, Fe^{3+}, As^{3+}, V^{3+}, NH_4^+, Na^+, K^+, Mg^{2+}, Co^{2+}	500
Cr^{3+}, Mn^{2+}, Ni^{2+}, VO^{2+}, Ag^+	200
Hg_2^{2+}, Hg^{2+}	100
CN^-	5

estimated concentration, respectively, M is the number of components, C_{ij} is the concentration of the ith component in the jth sample and is $\hat{C}_{ij}$ its estimation. The values of statistical parameters calculated in optimum number of factors for sulfide and sulfite in the prediction set are summarized in Table 4.

Selectivity. To study the selectivity of the proposed method, the effect of various ions on the determination of a mixture of 0.50 μg mL^{-1} each of sulfite and sulfide was tested under the optimum conditions. The tolerance limit was defined as the concentration of added ion causing less than ±3 relative error. The results are given in Table 5. As Table 4 shows, most of the cations and anions did not interfere on the simultaneous detrermiation of sulfite and sulfide by the proposed method even when present in 200- to 1000-fold excess over sulfite and sulfide. Therefore the method shows a good selectivity for the determination of sulfide and sulfite in mixture.

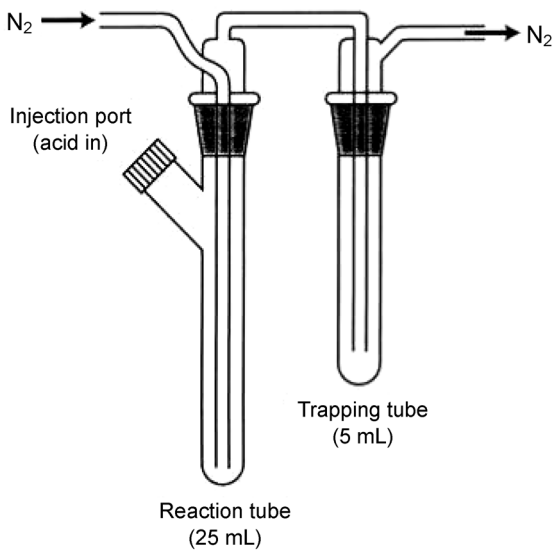

Figure 6. Gas-phase separation apparatus. It consists of reaction tube, trapping tube, gas dispersers and injection port.

Table 6. Simultaneous determination of sulfite and sulfide in water samples

samples	Sulfite (μg mL^{-1})		Sulfide (μg mL^{-1})	
	Added	Found[a]	Added	Found[a]
Whole blood	–	0.28 ± 0.07	–	0.11 ± 0.04
	0.10	0.41 ± 0.05	0.20	0.24 ± 0.05
	0.35	0.59 ± 0.03	0.10	0.18 ± 0.06
	0.50	0.81 ± 0.04	0.35	0.48 ± 0.08
Tap water	–	ND[b]	–	ND
	0.60	0.65 ± 0.02	0.20	0.19 ± 0.05
	0.50	0.55 ± 0.06	0.70	0.66 ± 0.03
	1.0	0.96 ± 0.07	0.40	0.37± 0.04
	0.72	0.75 ± 0.06	0.80	0.83 ± 0.02
	1.2	1.10 ± 0.03	0.50	0.48 ± 0.07
Spring water	–	ND	–	0.85 ± 0.04
	0.10	0.10 ± 0.02	1.0	1.83 ± 0.05
	0.50	0.56 ± 0.06	0.75	1.56 ± 0.02
	1.2	1.1 ± 0.05	0.050	0.90 ± 0.04
	0.1	0.12 ± 0.05	1.2	1.95 ± 0.06
	0.25	0.26 ± 0.07	0.50	1.31 ± 0.01
	0.70	0.75 ± 0.03	0.80	1.65 ± 0.05
	0.90	0.84 ± 0.02	0.20	1.04 ± 0.06

[a]Mean ± standard deviation for three determinations. [b]Not detected.

Application. To evaluate the analytical applicability of the proposed method, it was applied to the simultaneous determination of sulfite and sulfide in water samples and in whole human blood.

In order to separate sulfide and sulfite content of the whole blood a gas-phase separation apparatus was used (Figure 1).[35] The traps consist of two glass tubes, one for the test sample, which has an injection port into which acid is injected to release hydrogen sulfide and SO_2. The other tube is used to trap the hydrogen sulfide and SO_2 as anionic sulfide and SO_3^{2-} in 0.1 mol L^{-1} of sodium hydroxide solution. The two tubes are joined by a head unit, which enables H_2S and SO_2 gases evolved to be carried into the trapping solution. The design also allows the introduction of inert carrier gas (N_2) directly into the sample tube.

A 5 ml of 15 mol L^{-1} sulfuric acid solution was injected in reaction tube that contains 15 mL of human blood. The produced hydrogen sulfide and SO_2 was carried by the nitrogen flow from reaction tube into the trapping tube containing 5 mL of the trapping solution (0.1 mol L^{-1} NaOH). The hydrogen sulfide and SO_2 were quantitatively collected in the NaOH absorber. The pH of the solution was adjusted to about 7 by 0.2 M HNO_3 its sulfite and sulfide concentration was determined by the proposed method. The results are given in Table 6. The results show that the PLS-1 model is able to predict the simultaneous determination of sulfite and sulfide concentrations in such samples.

Conclusion. The above results show that PLS-1 is an excellent calibration method to simultaneous determination of sulfite and sulfide, based on the different in their reaction rates with Malachite Green. The partial least squares is a

powerful tool for the simultaneous determination of the analytes. The results in Table 6 show that PLS-1 can appropriately model multicomponent systems and predict unknown analyte concentrations with satisfactory results.

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