Combining Ultraviolet-Visible Spectrometry And Chemometrics For Simultaneous Determination Of Copper, Chrome And Nickel Ions In Water

Jiangjiang Wang, Jia Zhao, Xia Liu, Lijun Zhang, Qingyin Zhang and Yugao Guo

School of Environmental and Chemical Engineering, Tianjin Polytechnic University, Tianjin 300387, China

Abstract

Analysis of metal ions in environment is of great importance for evaluating the risk of heavy metal to public health and ecological safety. Amount of Cu^{2+}, Co^{3+} and Ni^{2+} can be traced by xylenol orange indicator when sensitive color reaction occurs at pH 5.8, but the absorption spectra of the formation of a ternary mixture of micelles overlap seriously. In this study, the experimental data of ultraviolet-visible spectroscopy were preprocessed by smoothing method which has good treatment effect through calculation and comparison. Then, a method for simultaneous determination of these three metal ions in water samples was developed by using partial least squares regression based on these treated data. The square of correlation coefficients of the independent validation was 0.9907, 0.9916 and 0.9957 for Cu^{2+}, Co^{3+} and Ni^{2+}, respectively. The results indicated that the partial least squares regression combined with ultraviolet-visible spectrometry could be utilized to simultaneous determination of trace metal ions in water.

Keywords

Heavy metal ions; partial least squares regression; spectrophotometry; simultaneous determination; ultraviolet-visible spectrometry; chemometrics.

1. Introduction

As we all know, spectrophotometry is widely applied due to its simple operation, accuracy and cost-effectiveness [1] in heavy metals determination filed. However, Spectrophotometry is hard to determine different compounds simultaneously. Therefore, the chemometrics method [2-4], which can maximize the information extracting from the calibration sample with strong data processing capabilities, was introduced into the simultaneous determination of different heavy metal ions. This study is mainly to achieve a goal of simultaneous detection of three metal ions. This study found that Cu^{2+}, Co^{3+}, Ni^{2+} with xylenol orange (XO) occurs highly sensitive color reaction, but the absorption spectrum was seriously overlapped. This paper not only studies XO and Cu^{2+}, Co^{3+}, Ni^{2+} color reaction, but also studies on the effect of buffer solution and reagent dosage on the reaction for the determination of Cu^{2+}, Co^{3+} , Ni^{2+} and XO spectrophotometry. Under this condition, the application of PLSR method is used to achieve a measurement of three components simultaneously.

2. Experimental Section

2.1 Reagents and sample preparation

Copper nitrate, Cobalt nitrate, Nickel nitrate (sailboat Chemical Reagent Co., Ltd. Tianjin, China) were of analytical grade. XO (Institute of Fine Chemicals retrocession, Tianjin, China) was of analytical grade. The water used was doubly distilled and deionized. Stock solutions of 1000 mg/mL of copper, cobalt and nickel were prepared from correspondent reagents with water as solvents. Sodium acetate buffer solution (pH=5.8) were prepared by mixing sufficient amount of acetic acid and sodium acetate. 0.2% XO solution (0.2 g XO solution dissolved in water volume to 100 mL flask).

In a 10.0 mL centrifuge tube, some standard solution of the Cu^{2+}, Co^{3+}, Ni^{2+} are placed and then pipetting distilled water to 2.5 mL. Then add sequentially 2.0 mL sodium acetate buffer solution and

1.0 mL 0.2% XO solution to the centrifuge tube. Each sample shakes for 5 min before measuring spectra. The various heavy metal ions within a certain range of concentrations are divided evenly into 50 groups, respectively. 50 groups of mixed solutions consisting of the three ions are randomly generated by matlab software. The concentration interval of each ion is 0.1 mg/L. The concentration range of the Cu^{2+}, Co^{3+}, Ni^{2+} are 0.1-5.0 mg/L, 0.1-5.0 mg/L, and 0.1-5.0 mg/L.

2.2 Spectral measurement

UV-Vis spectra of the samples were obtained with a TU-1901 double beam UV spectrophotometer (Beijing Purkinje General Instrument Co Ltd, China). The spectra were collected at a resolution of 1 nm, over the wave number range of 200-800 nm. Each spectrum is composed of 600 data points (reagent blank as a contrast).

2.3 Data Pretreatment

Confronted by drifting baseline or background in the spectra, signal processing techniques such as smoothing, standard normal variate (SNV) and multiplicative scatter correction (MSC), individually and in combinations, are usually used to obtain the optimized PLS models. Smoothing and derivatives are performed using the Savitzky-Golay algorithm [5], with the aim of reducing the fluctuating noise and removing baseline variations. SNV and MSC are known as baseline or background correction methods [6], and CWT serves to eliminate both the varying background and the noise [7-10]. In this study, we choose smoothing, SNV and MSC as the pretreatment methods.

2.4 Quantification modeling and evaluation

Quantitative analysis was performed by PLSR, because it is the most commonly used multivariate calibration method. The number of latent variables (LV) for PLSR model was determined by using Monte Carlo cross-validation (MCCV) combined with Osten's F criterion[11]. In the calculations, all the samples were divided into calibration and validation set by a ratio of ca. 2:1 using Kennard-Stone method [12]. Therefore, 33 samples were used as calibration set to construct the quantitative models, and the other 27 samples were used as validation set to evaluate the models. The performance of PLS regression models was evaluated in terms of the square of correlation coefficient (R^2) between the measured and predicted values and the root mean square error of cross validation (RMSECV), which was obtained by MCCV.

3. Results and Discussion

3.1 Chromogenic reaction

3.1.1 Maximum absorption

Absorption spectra of Cu^{2+}, Co^{3+}, Ni^{2+} with XO chromogenic reaction is seriously overlapped at pH 5.8 (Fig. 1) . Under the same conditions, the λ_{max} of Cu^{2+}, Co^{3+}, Ni^{2+} is 572, 579 and 579 nm, respectively. The λ_{max} of the mixed ions is 578 nm.

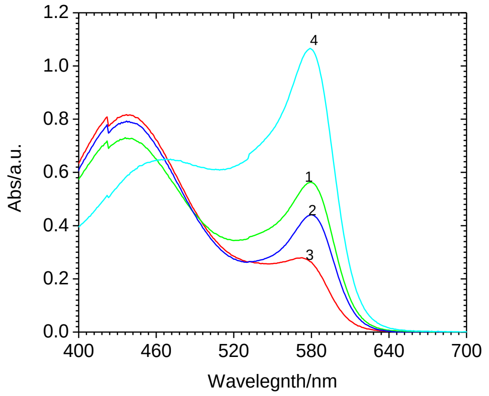

Fig. 1 The absorption spectra of different solution with XO and sodium acetate buffer solution as reagents, (1) Co3+: 1.0 ppm; (2) Ni2+: 1.0 ppm; (3) Cu2+: 1.0 ppm; and (4) mixed solution.

3.1.2 Effect of pH and amount

According to a certain proportion, sodium acetate and acetic acid were prepared to buffer solutions at different pH. Under the different pH conditions (reagent blank as a contrast), the absorbance of XO with metal ions shows a obvious difference (Fig. 2). In the range of pH 3.8-7.0, a greater change in absorbance was shown for each complex ion, except for a small change between 5.0 and 6.0.

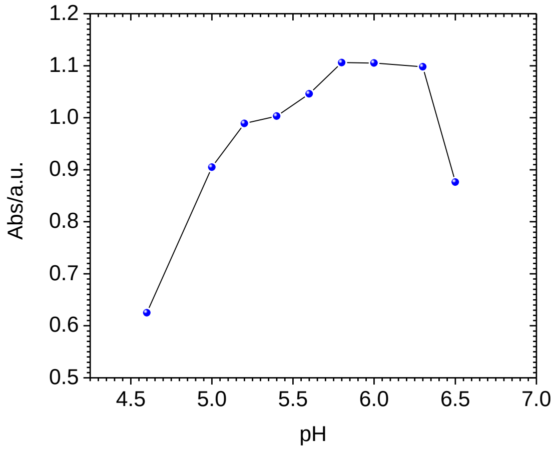

Fig. 2 Effect of pH of the three complex ions at the λmax=578 nm

Under the pH 5.8, different amount of the acetate buffer solution were prepared (reagent blank as a contrast). When the amount of the acetate buffer solution is between 1.5-2.5 mL, the absorbance of each complex ions is larger and constant (Fig. 3). When the amount is smaller than 2.0 mL, the color reaction is not complete, thus the reagent consumption was not enough; when the amount is larger than 2.0mL, reagent color is no significant change in the maximum absorbance, obviously that color agent reached saturation. so the amount of buffer solution of 2.0mL is preferred in this experiment.

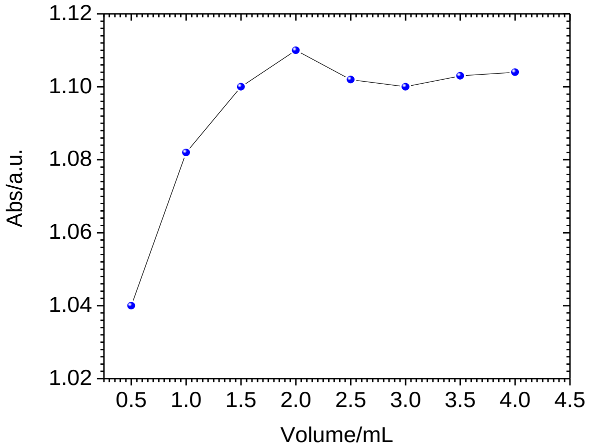

Fig. 3 Effect of the amount of the three complex ions at the λmax=578 nm (pH =5.8)

3.1.3 The amount of XO

Experimental results show that three kinds of mixed metal ions with XO occurs sensitive color reaction. After determining the pH and the amount of buffer solution, the amount of XO also affect absorbance of the solution. Under the different pH conditions (reagent blank as a contrast), each group is added different amount of XO .The range amount of XO is 0.3-2.0 mL (Fig. 4) .With the increase of the amount of reagents, the absorbance data of the complex is reached constantly. Since the amount of the complex metal ions with the reagent is sufficient, therefore the amount of XO is set as 1.0 mL in the following measurements.

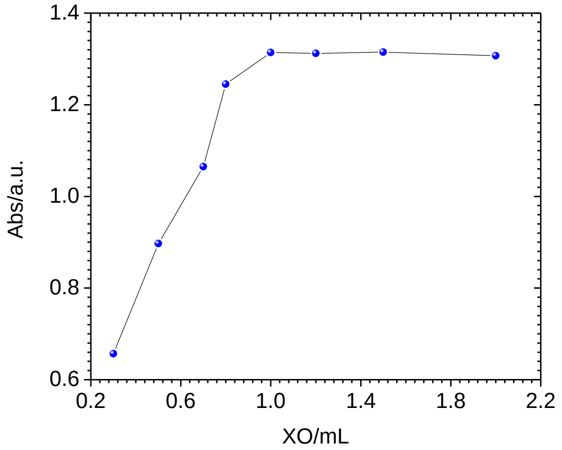

Fig. 4 Effect of the amount of XO of the three complex ions at the λmax=578 nm

3.2 PLS method of calculating

3.2.1 Grouping and test samples

50 groups of mixed solutions have joined into 2.0 mL buffer solution, 1.0 mL of 0.2% XO solution, after shaking for 5 min, then testing by UV spectrophotometer to obtain spectra of the UV-Vis spectra (Fig. 5). The absorption spectra of the formation of a ternary mixture of micelles overlap seriously. It cannot be quantified by means of the correction by chemometrics method.

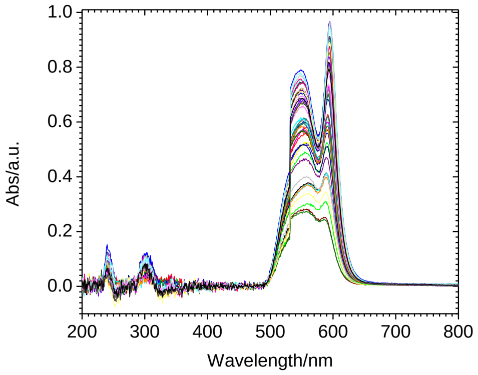

Fig. 5 Measured UV-Vis spectra of the 50 mixed samples

Table 1 PLS models and the results of cross validation.

Analyte	Preprocessing	LV numbers	*R^2*	*RMSEP*
Cu^{2+}	None	9	0.9858	0.2856
	SNV	9	0.9889	0.2446
	MSC	9	0.9895	0.2403
	Smoothing	8	0.9907	0.2310
Co^{3+}	None	5	0.9856	0.2854
	SNV	6	0.9901	0.2198
	MSC	6	0.9914	0.2108
	Smoothing	5	0.9916	0.2075
Ni^{2+}	None	5	0.9865	0.2789
	SNV	6	0.9898	0.2765
	MSC	6	0.9916	0.1326
	Smoothing	5	0.9957	0.1064

3.2.2 Effect of the pretreatment methods

The results obtained by three pretreatment methods: smoothing, SNV, MSC, are summarized in the lines of Table 1. The calculations use the full spectral data (200-800nm) to optimize the parameters for pretreatment. The models can be evaluated by the two parameters, a better model should have a higher correlation coefficient (R^2), and a lower root mean squared error of prediction (RMSEP). Smoothing removes noise, SNV and MSC correct the baseline, while the results of the three ions had a little differences, smoothing is the best. So we choose smoothing –PLS model.

3.2.3 Modeling and Computation

PLSR is a widely used method in chemometrics. In this contribution, PLSR was applied for modeling and prediction. OPUS-QUANT program in the OPUS 6.0 software package provided within the instrument was used. As described above, the 33 samples were used as calibration set to build the PLS models, and another 27 samples were used for validation of the methods.

As mentioned earlier, PLS is an optimal chemometric modeling method. The number of latent variable (LV) is the key step to determine PLS modeling process. LV is the reserved optimal model dimension of the original spectral data conversion to PLS space. If the LV number used in the model is small, which will cause under- fitting. While the number of selected principal components is too large, it will lead to over-fitting. Usually it takes the minimum value of RMSECV as the optimal number of the model.

Fig. 6 shows the optimal LV numbers for the three acceptable models content are 8, 5 and 5. The value of RMSECV is 0.48065, 0.33060, and 0.43012, respectively. After determining the optimal number of factors, those factors number are inputted into PLS main program to validate this model.

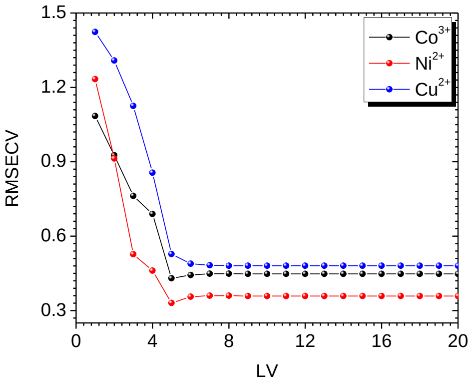

Fig. 6 Variation of the RMSECV with the number of LV for the three metal ions

3.2.4 PLSR model to predict

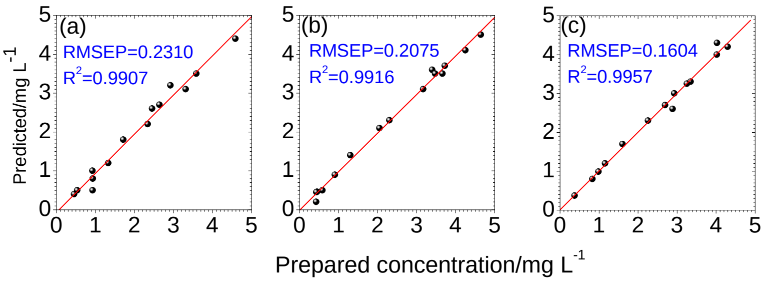

Fig. 7 Relationship between the prepared and predicted concentration of validation set by PLSR for Cu2+ (a), Co3+ (b) and Ni2+ (c)

Apparently, a better model should have a higher correlation coefficient (R^2), a lower RMSECV and a lower root mean squared error of prediction (RMSEP). In Fig. 7 (a)-(c), R^2 and RMSEP were also labeled in the figures in the concentration range of 0-5.0 mg/L. The linear equations and square of correlation coefficients are: Abs.=1.00731C_{Cu}–0.07213; Abs.=0.99155C_{Co}+0.01305 and

Abs.=0.99965C_{Ni}+0.00331for Cu^{2+}, Co^{3+} and Ni^{2+}, respectively. The RMSEP of the three ions are 0.2310, 0.2075 and 0.1604. Results show that PLS model combined with UV-Vis spectra for 16 detecting heavy metal ions in water is feasible.

4. Conclusion

In summary, Cu^{2+}, Co^{3+} and Ni^{2+} with xylenol orange (XO) indicator occurs sensitive color reaction at pH 5.8, and the amount of buffer solution and XO are 2.0 mLand 1.0 mL respectively. The square of correlation coefficients (R^2) of the independent validation are found as 0.9907, 0.9916 and 0.9957 for Cu^{2+}, Co^{3+} and Ni^{2+}, and the value of RMSEP are 0.2310, 0.2075, 0.1604, respectively. Results show that UV-Vis spectrometry combined with PLSR can be used for trace detection of heavy metal ions in water. Further works are still needed for to make the method widely used in practical analysis field.

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