Simultaneous Spectrophotometric Determination of Iron, Cobalt and Copper by Partial Least-Squares Calibration Method in Micellar Medium

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Abstract

Iron, cobalt and copper are metals, which appear together in many real samples, both natural and artificial. Recently a classical univariate micellar colorimetric method has been developed for determination of these metal ions.

The organized molecular assemblies such as micelles are used in spectroscopic measurements due to their possible effects on the systems of interest. The ability of micellar systems to solublize slightly insoluble or even very insoluble complexes and/or ligands has been used to enhance the analytical merit of the given methods. The ability of micelles to solublize complexes in aqueous solutions can eliminate the need for non-aqueous extraction step in a given analysis.

The simultaneous determination of Fe, Co and Cu was carried out as 1-nitroso-2-naphtol complexes in presence of aqueous solution of nonionic surfactant of Triton-X100. A partial least-squares multivariate calibration method for the analysis of ternary mixtures of Fe, Co and Cu was developed. For individual determinations, molar absorptivities and the limit of detection were obtained, respectively. The total relative standard error for applying the method on synthetic samples was 2.02%. The proposed method was also successfully when applied to the determination of Fe, Co and Cu in several synthetic alloy solutions.

Keywords: Iron; Cobalt; Copper; Partial least-square; Chemometrics; Determination.

Introduction

Iron, Cobalt and Copper are metals which appear together almost in all real samples, both natural and artificial. In most cases, the characterization of these samples includes the determination of their metal ion content. The need for Iron, cobalt and copper analysis in environmental and biochemical material has increased after reports on different roles of these metals in human heath and diseases (1, 2, 3).

The simultaneous determination of Iron, cobalt and copper has been studied in different samples and by using very different techniques. Iron, cobalt and copper have very similar chemical behavior, and they have been simultaneously determined mainly electrochemically and chromatographically. Several techniques such as X-ray fluorescence (4), atomic fluorescence spectrometry (5), polarography (6), chromatography (7), atomic absorption spectrophotometry (8), have been used for the simultaneous determination of these ions in different samples. Among the most widely used analytical methods are those based on the UV-visible spectrophotometry techniques, due to both the simplicity and rapidness of the method. (9-11). However, the simultaneous determination of these ions by the use of the traditional spectrophotometry techniques is difficult since, the absorption region and the superimposed curves are not suitable for quantitative evaluation. In most complex samples spectral overlap is often a serious problem because the information of

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each component obtained from the overlapping spectra is very limited and condition number of the absorbance coefficient matrix is too large to give satisfactory results. In most cases pretreatment of samples, physical separation and non-universal instrumentation are required. Recently, quantitative spectrophotometry has been greatly improved by the use of a variety of multivariate statistical methods such as classical least square (CLS) (12), inverse least square (ILS) (13), principal component regression (PCR) (14), and partial least square (PLS) (15). Multivariate calibrations are effective in spectrophotometric analysis because the simultaneous inclusion of multiple spectral intensities can greatly improve the precision and applicability. The widespread use of these methods is due to the proliferation of commercial software for laboratory computers and detectors capable of recording full spectra very rapidly.

Partial least square (PLS) modeling is a powerful multivariate statistical tool that has been successfully applied to the quantitative analysis of spectroscopic (16-20) and electrochemical (21) data. PLS is capable of being a full spectrum method and therefore enjoys the signal averaging advantages of other full-spectrum methods such as principal component regression (PCR) and classical least-square (CLS). PLS also has characteristics and advantages of inverse least-square (ILS) method, which is limited in the number of spectral frequencies that can be included in the analysis (17). The basic concept of PLS regression was originally developed by Wold (22, 23) and the use of PLS method in chemical analysis was also pioneered by Wold and coworkers (24). A particularly detailed study of multivariate calibration by PLS was carried out for spectrophotometric determination of metals (25).

1-nitroso-2-naphtol reacts with several metal ions such as iron, cobalt, copper and Vanadium to form colored metal complexes (26). This chelating agent has been used to determine several metal ions by ultraviolet-visible (UV-Vis) spectrophotometry. But these metal-1-nitroso-2-naphtol complexes do not dissolve in aqueous solution, so it is necessary to perform a solvent extraction. These complexes had been extracted by chloroform (26, 27) which was found to be carcinogenic and was later banned

by FDA for using in drug, cosmetic and food packaging products (29). Micellar systems are convenient to use because they are optically transparent, readily available and stable (30). The organized molecular assemblies such as micelles are used in spectroscopic measurements due to their possible effects on the systems of interest. In the field of metal ion complexation, at concentrations above the critical micelles concentration, (CMC), micelles form a ternary complex with advantageous properties, such as hyperchromic and bathochromic displacements, that can modify sensitivity of the method by affecting the interferences and matrix effects (31). The ability of micellar system to solubilize slightly insoluble or even very insoluble complexes and/or ligands has been used to enhance the analytical merit of given methods (32-34). The ability of micelles to solubilize complexes in aqueous solution can eliminate the need for non-aqueous extraction step in a given analysis (32, 35, 36). This reduces the cost and toxicity of the method.

Experimental

Reagents and solutions

All chemicals were of analytical-grade (Merck Co.). Double distilled water was used throughout. Standard Fe (III), Co (II), and Cu (II) solution were made with 100 μg ml^{-1} stock solution prepared using their metal nitrate salts (Merck, Co). Triton X-100 was used as a nonionic surfactant. Acetate buffer solutions (pH=4) were prepared by mixing 0.9 ml of 0.2 M sodium acetate with 41ml of the 0.2 M acetic acid and diluting to 100 ml with deionized water. For preparing the standard solution, one ml of 1-nitroso-2-naphtol (0.05 M), 2 g of Triton X-100 were added to a 100 ml volumetric flask and made up to the mark with acetate buffer (pH=4). All of the solutions were prepared fresh daily.

Apparatus

A GBC 40 Cintra model UV-Vis spectrophotometer equipped with a 1-cm quartz cell, a scan rate of 800 nm/min and slit width of 2 mm was used to measure absorbances of all analytical species. All spectral measurements

were performed using the blank solution as a reference. Measurement of pH was carried out on a metrohm 691 pH-meter using combined glass electrode. The computations were performed on a Pentium II computer. All the programs in the computing process were written in MATLAB® for Windows.

Procedures

Individual calibration

For the preparation of each standard solution 5 ml of micellar mixed reagents and appropriate amounts of the metal ion solution were added to 10 ml voltametric flask and made up to the mark with double distilled water. The concentration of iron, cobalt and copper were 0.1-4.0 μg/ml, 0.05-2.5 μg/ml and 0.05-6 μg/ml, respectively. The absorbances were measured at 420 nm, 425 nm and 408 nm, against a reagent blank for iron, cobalt and copper ions, respectively.

PLS calibration

Each standard, prediction and synthetic mixtures were prepared as follows:

5 ml of micellar mixed reagents and appropriate amounts of themetal ion solution were added to 10 ml voltametric flask and made up to the mark with double distilled water. Different amounts of iron, cobalt and copper were added from 100 μg/ml solution of the metal ion. Excess the 1-nitroso-2-naphtol was used to ensure quantitative formation of the complexes in the whole region of the calibration. The concentrations in these mixtures were in the range 0.1-3 μg/ml, 0.05-2 μg/ml and 0.05-3.5 μg/ml for iron, cobalt and copper respectively. The concentration ranges were chosen so that the absorbances obtained for all standard samples were not greater than 1.5. The compositions of the samples were randomly designed in order to obtain maximum information on each ion from the calibration procedure.

Results and discussion

The phenomenon of micellar solubilization of a water insoluble compound has great analytical significance. The solubilization technique has been employed for determination of many metal ions in aqueous solution with organic reagents (37, 38) and troublesome problems, such as undesirable precipitation associated with the determination, are avoided. 1-nitroso-2-naphtol is a chelating agent and has been used to determine several metal ions by ultraviolet-visible (UV-Vis) spectrophotometry but these complexes are water insoluble and therefore a solvent extraction step is necessary. Generally, chloroform is employed as the organic solvent (27, 28). This solvent is classified as a toxic and as an environmental pollutant (39) and has been listed as carcinogenic by the Environmental Protection Agency (EPA) (40) and Food and Drug administration (FDA) (29). When triton x-100 is used, the extraction process which is necessary in the absence of the micells, could be skipped. The 1-nitroso-2-naphthol concentration has been chosen to ensure complete solubilization and stabilization of metal ion complex.

The influence of pH value on the spectrum of each complex at a constant concentration was investigated separately and the pH=4 was chosen as an optimum pH value for simultaneous analysis of Fe, Co and Cu.

Individual calibration curves were constructed with several points for each metal ion.

Figure 1 shows absorbance versus metal ion concentration in the range of 0.05-6 μg/ml evaluated by linear regression. The molar absorptivities were 2.57×10^4 for Fe (420 nm), 4.62×10^4 for Co (425) and 2.04×10^4 for Cu (408), 1 $mol^{-1}cm^{-1}$. The intercept on the ordinates were negligible in all three curves. Limit of detection calculated as LOD=$3s_0$/slope, (where the s_0 is the standard deviation of the intercept on ordinate) was 0.06 μg/ml for Fe, 0.02 μg/ml for Co and 0.04 μg/ml for Cu.
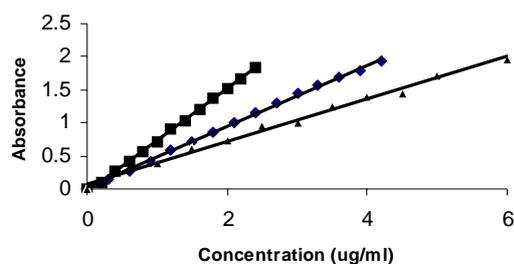
Figure 1. Individual calibration graphs for Fe λ=420 , r=0.9991, Co λ=425, r=0.9996 and Cu λ=408, r=0.9994
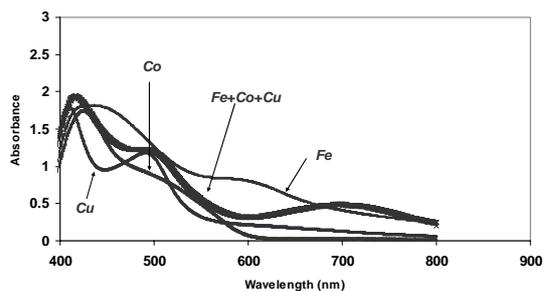
Figure 2.Absorption spectra of Metal ions solution .Curve for 2 μg/ml Fe(III),2 μg/ml Co (II),2 μg/ml Cu(II) and 1 μg/ml Fe(III)+1 μg/ml Co(II)+2 μg/ml Cu(II).

Figure 3. Plot of PRESS against the number of factors for Fe (III), Co (II) and Cu (II).

Figure 2 shows the absorption spectra for the individual metal complexes and the mixture of them. The first step in the simultaneous determination of different metal ions by PLS methodology involved constructing the calibration matrix for the ternary mixture Fe-Co-Cu. Forty five ternary mixtures were selected as the calibration set. Their composition was randomly designed for obtaining more information from calibration procedure. Under this condition, the calibration model was obtained. The calibration model was validated with 18 synthetic mixtures containing the metal ions in different proportions that were randomly designed. The results obtained are given in Table 1. To select the number of factors in PLS algorithm, a cross validation method, leaving out one sample at a time, was employed (17). For the mentioned sets of 45 calibration spectra, PLS1 calibration on 44

calibration spectra was performed and, using this calibration, the concentration of the sample left out during the calibration process was performed. This process was repeated 45 times and each sample had been left only once. The concentration of each sample was then predicted and compared with the known concentration of this reference sample, the prediction residual sum of squares (PRESS) was calculated. Figure 3 shows a plot of PRESS against the number of factors for each individual component. For finding the smallest model (fewest number of factors), the F-statistic was used to carry out the significance determination. The optimal number of factors for Fe, Co and Cu was obtained 4, 4 and 5, respectively.

In this work 18 synthetic test samples (Table 1) were analyzed with the suggested method. The prediction results are also given in this

Table1. Composition of synthetic Samples, their Prediction by PLS Model, and Statistical Parameters for the System

	Concentration								
	Synthetic			Prediction			Recovery %		
	Fe	Co	Cu	Fe	Co	Cu	Fe	Co	Cu
1	0.01	1.47	0.59	0.01	1.44	0.62	100.0	98.0	98.0
2	1.77	1.03	2.34	1.75	1.03	2.36	98.9	100.0	101.1
3	2.47	1.63	1.75	2.46	1.66	1.76	99.6	101.8	102.3
4	0.40	0.48	1.98	0.43	0.48	1.97	107.5	100.0	93.0
5	1.91	1.03	2.51	1.93	1.00	2.50	101.0	97.1	96.1
6	0.91	1.11	3.79	0.92	1.11	3.76	101.1	100.0	98.9
7	0.85	1.46	3.75	0.87	1.47	3.76	102.4	100.7	98.4
8	2.32	1.04	3.00	2.44	1.06	2.98	105.2	101.9	96.9
9	1.26	1.61	3.40	1.29	1.62	3.42	102.4	100.6	98.3
10	1.10	0.98	3.68	1.10	0.99	3.71	100.0	101.0	101.0
11	1.22	1.23	1.88	1.24	1.25	1.99	101.6	101.6	100.0
12	2.93	0.80	3.77	2.97	0.80	3.79	101.4	100.0	98.7
13	1.92	0.71	2.12	1.92	0.72	2.30	100.0	101.4	101.4
14	0.01	1.47	0.59	0.01	1.48	0.60	100.0	100.7	100.7
15	0.44	1.28	2.57	0.46	1.29	2.55	104.5	100.8	96.4
16	0.61	1.70	0.66	0.65	1.70	0.69	106.6	100.0	93.8
17	0.91	1.11	3.79	0.93	1.20	3.77	102.2	108.1	105.8
18	0.61	1.70	0.66	0.59	1.73	0.66	96.7	101.8	105.2
Mean Recovery							101.7	100.9	99.2
[a]RSE%							2.41	2.12	2.00
[b]RSE Total								2.10	

[a] Calculated according to the equation 1

[b] Calculated according to the equation 2

table. The prediction error of single component in the mixture was calculated as the relative standard error (RSE) of the prediction concentration:

$$\text{RSE (\%)} = 100 \times (\Sigma \, (\hat{C}_j - C_j)^2 / \Sigma \, (C_j)^2)^{1/2}$$

(Equation 1)

Where N is the number of samples, $\hat{C}_j$ is the concentration of the component in jth mixture and C_j is the estimated concentration. The total prediction error of N samples is calculated as follows:

$$\text{RSE (\%)} = 100 \times (\Sigma \, \Sigma \, (\hat{C}_{ij} - C_{ij})^2 / \Sigma \, \Sigma \, (C_{ij})^2)^{1/2}$$

(Equation 2)

Where C_{ij} is the concentration of the ijth component in the ijth sample and C_{ij} is its estimation. Table 1 also shows reasonable single and total relative error such a system.

For analyzing the possible interference, the influence of several ions was tested, including those that most frequently accompany Fe, Co and Cu in real samples. The effect of interfering ions at different concentrations on the absorbency of a solution containing 1 μg ml^{-1} of each analyte was studied. An ion was considered to interfere when its presence produced >5% variation in absorbency of the sample. This increment of absorbency was evaluated at three wavelengths, 420, 425 and 408 (corresponding to the maximum absorption of Fe, Co and Cu complexes respectively), to establish the different effect of the interfering ions on each analyte. Among the interfering ion tested, CO_3^{2-}, CN^-, F^-, I^-, Br^-, CH_3COO^-, NO_3^-, Ba^{2+}, Mg^{2+}, Ca^{2+}, Li^+, Na^+, Zn^{2+}, Mo^{6+} and Al^{3+} did not interfere at concentrations 1000 times higher than those of the analytes.

The proposed calibration method was applied to determine the concentration of Fe, Co and Cu in several artificial synthetic samples made by mineral water. The results are shown in Table 2. The good agreement between these results and the known values indicates the successful applicability of proposed method for

Table 2. Actual Composition and Calculated Concentration of Iron, Cobalt, and Copper in Synthetic Mixture of Some Alloys (mineral water)

Alloy solution	Composition of Synthetic mixture μg/ml			Found μg/ml		
	Fe	Co	Cu	Fe	Co	Cu
Damavand	2.5	1	3.5	2.51	1.01	3.52
Sabalan	2.0	1.5	4	2.01	1.52	3.98
Tap water	3.0	0.5	2.5	3.01	0.51	2.53

simultaneous determination of Fe, Co and Cu in complex real samples.

The most important aspect of this work is the feasibility of simultaneous trace determination of Fe, Co and Cu as 1-nitroso-2-naphtol complexes in an aqueous solution produced by the presence of nonionic micelles of Triton X-100. No extraction step is needed and hence the use of organic solvents, which are generally toxic pollutants, is avoided. The proposed PLS1 model is very suitable for simultaneous determination of iron, cobalt and copper. It can be employed to analyze the artificial complex samples made by mineral water.

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