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Flow-injection chemiluminescence simultaneous determination of cobalt(II) and copper(II) using partial least squares calibration

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Abstract

A flow-injection chemiluminescence (CL) system is proposed for simultaneous determination of Co^{2+} and Cu^{2+} using partial least squares (PLS) calibration. This method is based on the fact that both Co^{2+} and Cu^{2+} catalyse the CL reaction of luminol-H_2O_2, and that their kinetic characteristics of Co^{2+} and Cu^{2+} are significantly different in the luminol-H_2O_2 system. The CL intensity was measured and recorder at different reaction times of luminol-H_2O_2—Co^{2+}—Cu^{2+}, and the obtained data were processed by the chemometric approach of partial least squares. The experimental calibration set was composed of 16 sample solutions using an orthogonal calibration design for two component mixtures. The proposed method offers the potential advantages of high sensitivity, simplicity and rapidity for Co^{2+} and Cu^{2+} determination, and was successfully applied to the simultaneous determination of both analytes in real water sample. The present paper demonstrated that the simultaneous determination of two metal ions without any prior separation has been possible using flow-injection CL system.

Keywords: Flow-injection; Chemiluminescence; Partial least squares; Simultaneous determination; Co^{2+} and Cu^{2+}

1. Introduction

Chemiluminescence (CL) is known to be a powerful and important analytical technique because the analytical performance of CL detection is better than that of other common spectroscopic detection methods, such as spectrophotometry and fluorescence, higher sensitivity, lower detection limits and wider linear ranges can be achieved with simpler instrument [1]. However, a limitation to widespread application of this technique is often poor selectivity of the CL detection itself because many coexisting substances can react with luminol or other CL reagents to give light emission [2]. Many analysts made great efforts to improve selectivity of CL or simultaneous determination, especially for luminol CL system. Pre-treatment or separation procedures are usually required for the selective determination in flow-injection CL analysis. The use of masking agents [3], membrane phase separator [4], anodic stripping voltammetry [5], solvent extraction [6] or discrete sample clean-up with ion exchange resin [7] has been reported. For simultaneous determination of multicomponent mixture, most CL systems were combined with high-performance liquid chromatography [8,9], gas chromatography [10], or capillary electrophoresis [11–13]. The CL systems used as postcolumn detectors have also met their problems: e.g., liquid chromatography needs the eluent, which often is a mixture of organic solvent and salts, and this eluent is always incompatible with the CL condition so as to decrease CL signal; in order to provide highly efficient collection of the CL, a CL cell must be specially designed, but such a cell is not commercially available. Thus, the development of new CL method, that allows the simultaneous determination without previous separations of these compounds, is a relevant subject of research.

In recent years, the use of some analytical methods combined with multivariate calibration can be considered a promising, faster, direct and relatively less expensive alternative for the multicomponent analysis of mixture [14]. In this kind of situation, where the direct determination of an analyte is difficult due to the presence of one or several other constituents, instead of eliminating the interfering species, e.g., by a separation procedure, the use of multivariate calibration makes possible the quantification of these interferences along with the analyte. Partial least squares (PLS) modelling, which was developed and

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introduced into chemistry by Wold et al. in 1983 [15], is one of the powerful multivariate statistical tool that has so far been most frequently applied to the UV–vis spectrophotometry [16–18], spectrofluoriometry [19–21], near infrared spectrometry [22,23] and electroanalytical method [24] for the multicomponent analysis of mixture without separation procedure. However, very few reports have described the application of PLS to CL simultaneous determination [25,26]. The main reason is that the intensity detected and recorded in CL analysis is a total intensity at all the wavelengths because there are not any spectroscopes in the common CL instrument. So the aid of spectral discrimination (such as absorbance-wavelength in UV–vis spectrophotometry) is not obtained for the simultaneous CL determination. If the kinetic characteristics of the analytes in the detection system are different, some compound mixture can be resolved obtaining time-intensity curves. Traditionally, batch and continuous flow methods are two basic sampling-injection modes for CL analysis. In the batch mode, CL reactants are rapidly mixed and the resulting intensity measured as a function of time. This method has the advantages of high sensitivity and minimizes reagent consumption. However, the CL intensity may be subject to poor precision due to variations in mixing, particularly if the reaction is fast. In the flow-injection CL analysis with high reproducibility, the stopped-flow technique is required to retain the emitting solution in the flow cell in order to obtain the whole profiles of CL intensity against time. However, the too frequent stop and start of pump affect the reproducibility of analytical data; the reaction mixture is not homogenized during stopped-flow course, which will influence the reaction; the analysis efficiency decreases because of the relative long stopped-flow time [26].

The pollution of water with transition-metal ions has increased dramatically in recent years as a consequence of the expansion of industrial activities. Among the transition-metal ions, cobalt(II) and copper(II) always appear together in water sample, and Co^{2+} and Cu^{2+} are toxic when their concentrations in water exceed certain levels. Therefore, a rapid and convenient method for their simultaneous analysis in natural water samples has attracted much attention. The CL method has successfully been applied to simultaneous determination of Co^{2+} and Cu^{2+}. Lu et al. suggested the flow-injection CL method coupled with ion chromatography to simultaneous determination of Co^{2+} and Cu^{2+} [27]. Time-resolved CL emissions have also been reported for simultaneous determination of Co^{2+} and Cu^{2+} [28]. In this paper, a simple flow-injection CL system combined with PLS calibration is presented to synchronously determinate Co^{2+} and Cu^{2+}. This method is based on the fact that both Co^{2+} and Cu^{2+} catalyse the CL reaction of luminol-H_2O_2, and that their CL kinetic characteristics of Co^{2+} and Cu^{2+} are significantly different in the luminol-H_2O_2 system. Instead of the stopped-flow technique usually used in flow-injection kinetic analysis, the CL kinetic profile is obtained by simple changing position of detected-signal point, according to the fact that the reaction time depends on the distance between the mixed-reagents point and the detected-signal point in a flow system with a constant flow rate. The CL intensity of luminol-H_2O_2–Co^{2+}–Cu^{2+} was measured and recorded on the different detected-signal points, and the obtained data were processed by PLS. Compared with the reported CL methods for simultaneous determination of Co^{2+} and Cu^{2+} [27,28], this method offers the potential advantages of simplicity, rapidity and sensitivity for Co^{2+} and Cu^{2+} determination.

2. Theoretical background

Assuming, n analytes react with a common reagent R and give the same product P. In the presence of excess reagents, the intensity of light emission is proportional to the metal catalyst concentration [29]. The CL intensity (I) measurement versus reaction medium pH can be expressed as:

$$I_j = b_{0j} + \sum_{i=1}^{n} b_{jj}c_i \quad (j = 1, 2, \ldots, s) \tag{1}$$

where b_{jj} is the proportional coefficient for component i at point of time j, and b_{0j} is the corresponding background. Eq. (1) can further be simply written as:

$$I_j = \sum_{i=1}^{n} b_{jj}c_i \quad (j = 1, 2, \ldots, s) \tag{2}$$

if m standard samples are prepared, Eq. (2) can be extended and expressed in matrix form:

$$I_{m\times s} = C_{m\times(n+1)}B_{(n+1)\times s} \tag{3}$$

where the first row in matrix B represents the background vector. According to this equation it is possible to determine the component by suitable chemometric method. In this work, the experimental datum were collected from experiments, then were processed by PLS calibration method.

PLS is a multivariate calibration model, which involves a two-step procedure: (1) calibration, where the relation between response and reference component concentrations is established from a set of standard samples and (2) prediction, in which the calibration results are employed to estimate the component concentrations in unknown samples. In the PLS model, all model parameters are optimised for the determination of each analytes. During the model-training step, the calibration data are decomposed by an iterative algorithm, which correlates the data with the calibration concentrations using a so-called ‘inverse’ model. This provides a set of regression coefficients to be applied to a new sample.

3. Experimental

3.1. Chemical and reagents

All chemicals were of analytical grade and used without further purification. The water used throughout was deionised and double distilled.

A 5×10^{-2} mol/l luminol stock solution was prepared by dissolving 9.32 g of luminol in 20 ml of 0.01 mol/l NaOH and then dilution to 1 l with water. Luminol solution was stored in the dark for 24 h prior to use to ensure that the reagent properties had stabilized. H_2O_2 solution (4×10^{-2} mol/l) was prepared

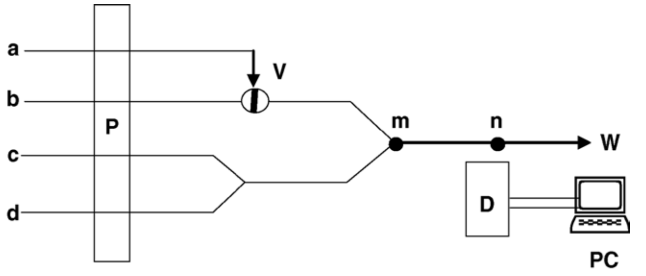

Fig. 1. Schematic diagram of CL flow system: (a) sample; (b) H_2O; (c) H_2O_2; (d) luminol basic solution; (*m*) mixed-reagents point; (*n*) detected-signal point; P: peristaltic pump; V: injection-valve; W: waste; D: detector; PC: personal computer.

daily from the stock solution by further dilution just before use. 1×10^{-4} g/ml of Co^{2+} and Cu^{2+} stock solutions were prepared by dissolving their hydrochloric salts (Xi'an Chemical Reagent Company, Xi'an, China) in water, respectively. A working standard solution was freshly prepared by diluting the stock solution with water.

3.2. Apparatus

The flow system used in this work is shown in Fig. 1. A peristaltic pump (Zhejiang Xiangshan Shipu Haitian Electronic Instrument Plant, China) was used to deliver all flow streams at a flow rate of 2.0 ml/min (per tuber). PTFE tubing (0.8 mm i.d.) was used as connection material in the flow system. A black plate with a hole (2 mm × 2 mm, used as detected-signal point) in the centre was placed on the window of photomultiplier (PMT). The straight PTFE tubing (length: 20 cm, i.d.: 0.8 mm) was used as CL flow-cell through the detected-signal point (*n*). Sample solution (150 μl) was injected by a six-way valve into the water carrier stream, and then merged just prior to reaching a flow cell with the stream of luminal and H_2O_2 at the mixed-reagents point (*m*). The CL signal produced at *n* point of the flow cell was collected with a CR-105 PMT (Hamamatsu, Japan) of the ultra-weak Chemiluminescence Analyzer (Institute of Biophysics, Chinese Academy of Sciences, Beijing). The signal was recorded using an IBM-compatible computer, equipped with a data acquisition interface. Date acquisition and treatment were performed with BPCL software running under Windows 95. The data pre-treatment was done with MATLAB for windows (Mathworks, version 6.1). The PLS program for calibration prediction and experimental design was written in MATLAB according to the algorithm described by Ni [14].

3.3. Procedure

As shown in Fig. 1, flow lines were inserted into analyte (a standard mixture solution or a sample mixture solution of Co^{2+} and Cu^{2+}), carrier solution, H_2O_2 solution and basic luminol solution, respectively. The pump was started to wash the whole flow system until a stable baseline was recorded. Then a 150 μl volume of mixed solution of Co^{2+} and Cu^{2+} was injected into the carrier stream. The stream was merged with luminol and H_2O_2 at point *m*, producing CL emission. The signal at point *n* was recorded using an IBM-compatible compute connected to the PMT. When the reaction conditions were optimised, the CL relative intensity corresponded to the normalized maximum light intensity. For univariate calibration, the CL intensity of Co^{2+} (or Cu^{2+}) standard solution was detected under the optimum conditions. For multivariate calibration, the CL intensity of each bicomponent mixture solution was detected at the distance between *m* and *n* of 0, 3, 6, 9 and 12 cm, respectively.

4. Results and discussion

4.1. Kinetic profile of CL reaction of luminol-H_2O_2–Co^{2+} (or Cu^{2+})

In the presence of a catalyst, luminol is oxidised by H_2O_2 in basic solution to form 3-aminophthalate in an excited state, which exhibits an intense luminescence ($\lambda_{max} = 425$ nm). In the batch mode, the CL emission describes a typical response curve (intensity versus time). The response curve corresponds to a first-order consecutive sequence: formation and destruction of light emitter [30]. Some metal ions (such as Co^{2+}, Cu^{2+} and Cr^{3+}) can increase the reaction rate. The rate-increasing effects have been better designated as promotions than catalytic effects because the rate-increasing species are consumed during the reaction in most cases [31]. The response curve depends on not only some experimental factors (such as pH and mixing rate), but also metal ion present in the system. When the experimental parameters are kept constant, the response curve is a function of metal ion. The preliminary experiment showed that the intensity-time curves of Co^{2+} and Cu^{2+} are different in luminol-H_2O_2–CL system. So, Co^{2+} and Cu^{2+} can be resolved based on their different kinetic characteristics. In order to obtain good reproducibility and high analysis efficiency, a flow-injection mode was used. In flow-injection analysis, the sample volume and flow rate affect time-based measurements. Based on the previous studies on the well-known luminol-H_2O_2–Co^{2+}/Cu^{2+} [31], we selected a sample volume (150 μl) and a flow rate (2 ml/min). Furthermore, we designed a special CL detection installation, by which the CL signal at only one point along the CL reaction mixing tube can be detected. As shown in Fig. 1, *m* is the beginning point of mixed-reagents and *n* is detected-signal point. In this flow system, a change in reaction time was achieved by modifying the distance between *n* and *m*. Fig. 2 shows the kinetic profile of Co^{2+} or/and Cu^{2+} in this luminol-H_2O_2 system. The experimental result showed that the reaction rate of luminol-H_2O_2–Co^{2+} was different from that of luminol-H_2O_2–Cu^{2+} on the distance between *m* and *n* of 0, 3, 6, 9, and 12 cm. So, for multivariate calibration, the CL intensity of each mixture solution of Co^{2+} and Cu^{2+} was detected at a distance between mixed-reagents point *m* and detected-signal point *n* of 0, 3, 6, 9, and 12 cm, respectively. Based on the difference in the rate between the two reactions, Co^{2+} and Cu^{2+} can be determination synchronously. Furthermore, synergy was observed when two catalysts acted simultaneously. It can be seen (Fig. 2) that the light intensity response of the mixture of Co^{2+} and Cu^{2+} was lower than the sum of the intensities recorded for each individual catalyst.

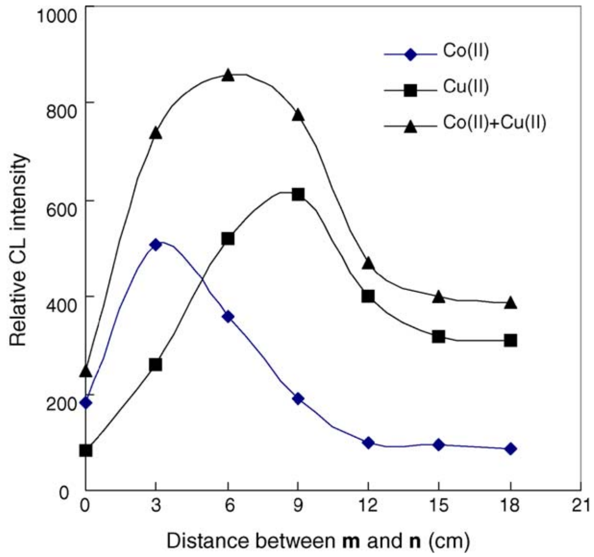

Fig. 2. Kinetic profile of luminol-H_2O_2 catalyzed by Co^{2+} or/and Cu^{2+}. Luminol, 5×10^{-4} mol/l; H_2O_2, 8×10^{-3} mol/l; Cu^{2+}, 2×10^{-6} g/ml; Co^{2+}, 2×10^{-8} g/ml.

4.2. *Optimisation of reaction condition*

Different chemical parameters were optimised. According to initial experiments, most critical variables were chosen. The studied range was selected based on the influence of variable on the CL signal. The optimisation criterion was the maximum signal and maximum repeatablility.

As the luminescence reagent in this system, luminol concentration affects the response. The effect of the luminol concentration was investigated. The result showed that the optimal concentration of luminol was 5×10^{-4} mol/l.

The experiment showed that below 8×10^{-3} mol/l H_2O_2, the CL intensity was proportional to the H_2O_2 concentration, which effect has been used to analysis H_2O_2 [32], and further increase in H_2O_2 concentration did not appreciably increase light emission. The high concentration of H_2O_2 could produce the obvious bubbles in the stream, which interfered in the detection of the CL signal in the system. A 8×10^{-3} mol/l H_2O_2 was selected for all subsequent experiments.

In view of the nature of luminol CL reaction, which is more favored under basic condition, NaOH was added to the luminol solution and used as the medium of the CL system. The effect of NaOH concentration in the range of 0.001–0.009 mol/l was investigated. It was found that the optimal NaOH concentration was 0.004 mol/l. Thus, the system was operated at 0.004 mol/l NaOH throughout this study.

4.3. *Univariate calibration*

Under the optimum conditions described above and the distance between *m* and *n* of 4 cm, the calibration graph of emission intensity versus Co^{2+} concentration was linear in the range 0.0002–0.4 μg/ml and the detection limit was 0.08 ng/ml (3σ). The calibration graph of emission intensity versus Cu^{2+} concentration was linear in the range 0.02–20 μg/ml and the detection limit was 6 ng/ml. The relative standard deviations ($n = 11$) were 4.4% for 0.02 μg/ml Co^{2+} and 3.2% for 2 μg/ml Cu^{2+}, respectively.

Table 1
Concentration data for different mixtures used in the calibration of Co^{2+} and Cu^{2+}

Mixture	Co^{2+} (μg/ml)	Cu^{2+} (μg/ml)
1	0.0010	0.8
2	0.0010	2.0
3	0.0010	6.0
4	0.0010	10.0
5	0.0080	0.8
6	0.0080	2.0
7	0.0080	6.0
8	0.0080	10.0
9	0.0200	0.8
10	0.0200	2.0
11	0.0200	6.0
12	0.0200	10.0
13	0.0600	0.8
14	0.0600	2.0
15	0.0600	6.0
16	0.0600	10.0

4.4. *Multivariate calibration*

Multivariate calibration methods such as PLS require a suitable experimental design of the standard belong to the calibration set in order to provide good prediction. Two sets of standard solutions were prepared. The calibration set consisting of 16 standards with different concentrations of Co^{2+} and Cu^{2+} following a two-factorial design (4^2) was used. The first one refers to Co^{2+} concentration and the second to Cu^{2+} concentration. Their concentrations are shown in Table 1. The CL intensity of each binary mixture solution was detected at distance between *m* and *n* of 0, 3, 6, 9, and 12 cm, respectively. An experimental calibration data matrix size 16 (number of samples) × 4 was prepared.

4.5. *Selection of optimum number of factors*

One of the most important key factors in the construction of PLS model is the selection of the number of significant factors. Generally a cross-validation method, leaving out one sample at a time was used [16]. With the set of 16 calibration mixtures, the PLS calibration was carried out for 15 mixtures and the concentration of the compounds predicted for the sample left out during calibration. This process was repeated 16 times until each calibration sample had been left out once. The predicted concentration of the compounds in each sample was compared with the known concentration of the compound in this reference sample, and the predicted error sum of squares (PRESS) was calculated. The PRESS was calculated in the same manner each time, and a new factor was added to the PLS model. One reasonable choice for the optimum number of factors would be the number (designated as h^*) that yields the minimum PRESS. However, using the number of factors that yields the minimum

Table 2
Prediction results for the synthetic mixture of Co^{2+} and Cu^{2+}

Synthetic mixture no.	Cu^{2+} (μg/ml)		Co^{2+} (μg/ml)	
	Added	Found	Added	Found
1	0.8	0.9	0.0060	0.0061
2	2.0	2.0	0.0050	0.0044
3	4.0	4.1	0.0080	0.0081
4	10.0	9.9	0.0040	0.0045
5	6.0	6.1	0.0200	0.0219
6	4.0	4.2	0.0200	0.0213
7	2.0	1.9	0.0400	0.0408
8	1.0	1.0	0.0600	0.0590

PRESS, h^* (the minimum PRESS value in the plot of PRESS versus number of factors) leads to overfitting. A better criterion for selecting the optimum number of factors is comparing the PRESS from a model with a factor less than h^*. The F-statistic was used to determine significant probability. Haaland and Thomas empirically determined that F-ratio probability of 0.75 is a good choice [33]. So, we also selected the optimum number of factors for the PRESS values of the F-ratio probability, which drops below 0.75. The maximum number of factors used to calculate the optimum PRESS was selected as 9 (half the number of standard plus one) [33]. The PRESS values are optimum at the number of 2 for both Co^{2+} and Cu^{2+}.

The binary synthetic mixtures of Co^{2+} and Cu^{2+} were analyzed by the proposed PLS calibrated method and prediction results are listed in Table 2.

4.6. Statistical parameters

For the optimised model, three parameters were selected to test the prediction ability of the chemometric model for each component. The root mean square difference (RMSD), the square of the correlation coefficient (R^2) and the relative error of prediction (REP), which can be calculated for each component as:

$$\mathrm{RMSD} = \left[\frac{1}{n}\sum_{i=1}^{n}(\hat{c}_i - c_i)^2\right]^{0.5} \quad (4)$$

$$R^2 = \frac{\sum_{i=1}^{n}(c_i - \bar{c}_i)^2}{\sum^{n}(c_i - \bar{c}_i)^2} \quad (5)$$

$$\mathrm{REP\%} = \left(\frac{100}{\bar{c}_i}\right)\left[\frac{1}{n}\sum_{i=1}^{n}(\hat{c}_i - c_i)^2\right]^{0.5} \quad (6)$$

where c_i is the true concentration of the analyte in the sample i, $\hat{c}_i$ represented the estimated concentration of the analyte in the sample i, $\bar{c}_i$ is the mean of the true concentration in the prediction set, and n is the total number of sample used in the prediction set. The RMSD, REP, R^2 and the number of factors are summarized in Table 3. The obtained values of the statistical parameters show the ability of the chosen method for determination of analytes simultaneous.

Table 3
Statistical parameters of the optimisation matrix using the PLS model

Sample	Number of factor	RMSD	REP%	R^2
Co^{2+}	2	0.0010	4.77	0.9837
Cu^{2+}	2	0.1061	2.85	0.9779

Table 4
Determination of Co^{2+} and Cu^{2+} in spiked spring water

Sample no.	Added (μg/ml)		Found (μg/ml)	
	Cu^{2+}	Co^{2+}	Cu^{2+} (%)	Co^{2+} (%)
1	5.0	0.0080	5.2 (104)[a]	0.0088 (110)[a]
2	2.5	0.0100	2.4 (96)	0.0110 (110)
3	0.9	0.0350	0.9 (100)	0.0340 (97)

[a] The values in parentheses refer to the recovery.

4.7. Interference study

The influence of foreign species was investigated by analyzing a standard mixture solution of 6×10^{-8} g/ml Co^{2+} and 1×10^{-7} g/ml Cu^{2+}, to which increasing amounts of interfering species were added. The tolerable limit of a foreign species was taken as a relative error not greater than 5%. The experimental result showed that Cr^{3+}, Fe^{2+} and Fe^{3+} were main cationic interferences as result of their high catalytic effect on the luminol-H_2O_2 system [34], and other common cations (such as Mn^{2+}, Ni^{2+}) did not seriously interfere with the detection of Co^{2+} and Cu^{2+} because Co^{2+} and Cu^{2+} are the excellent catalysts for luminol-H_2O_2 system [35]. The interference of Cr^{3+} and Fe^{3+} could be eliminated by adding 0.05 mol/l oxalate because Cr^{3+} and Fe^{3+} could form the stable complexes $Cr(Ox)_3{}^{3-}$ and $Fe(Ox)_3{}^{3-}$, respectively [27]. The effect of Fe^{2+} can be ignored because Fe^{2+} is very unstable and there is few Fe^{2+} present in water sample.

4.8. Application of the model to water sample

The proposed method was applied for the determination of Co^{2+} and Cu^{2+} in three spiked samples of spring water obtained from different factories. In order to evaluate the validity of the proposed method for the simultaneous determination of Co^{2+} and Cu^{2+}, recovery studies were carried out on samples to which known amounts of Co^{2+} and Cu^{2+} were added. The results are given in Table 4. As can be seen, the prediction ability of the model for the two analytes in real matrix is satisfactory.

5. Conclusion

The present paper demonstrated that the simultaneous determination of two metal ions (Co^{2+} and Cu^{2+}) without any prior separation has been possible using flow-injection CL system combined with PLS calibration. Moreover, the model can be readily adapted to three or four metal ions (Cr^{3+}, Fe^{3+}, Co^{2+} and Cu^{2+}) based on their difference of kinetic characteristics in luminol-H_2O_2 CL system. Our further work on the simultaneous determination of to three or four metal ions is in progress.

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References

[1] A. Roda, M. Guardigli, E. Michelini, M. Mirasoli, P. Pasini, Anal. Chem. 75 (2003) 462A.

[2] K. Robards, P.J. Worsfold, Anal. Chim. Acta 266 (1992) 147.

[3] Q. Lin, A. Guiraum, R. Escobar, F.F. De la Rosa, Anal. Chim. Acta 283 (1993) 379.

[4] J.R. Gord, G. Gordon, G.E. Pacey, Anal. Chem. 60 (1988) 2.

[5] W. Qin, Z. Zhang, H. Liu, Anal. Chem. 70 (1998) 3579.

[6] T. Fujiwara, I.U. Mohammadzai, K. Murayama, T. Kumamaru, Anal. Chem. 72 (2000) 1715.

[7] B. Li, Z. Zhang, Y. Jin, Sens. Actuators B 72 (2001) 115.

[8] P. Appelblad, T. Jonsson, T. Backstrom, K. Irgum, Anal. Chem. 70 (1998) 5002.

[9] M. Derbyshire, A. Lamberty, P. Gardiner, Anal. Chem. 71 (1999) 4203.

[10] C. Hao, P.B. Shepson, J.W. Drummond, K. Muthuramu, Anal. Chem. 66 (1994) 3737.

[11] A.M. Garcia Campana, W.R.G. Baeyens, Y. Zhao, Anal. Chem. 69 (1997) 83A.

[12] J. Ren, X. Huang, Anal. Chem. 72 (2001) 2663.

[13] B. Huang, L. Zhang, J. Li, J. Cheng, Anal. Chem. 68 (1996) 2366.

[14] Y. Ni, Application of Chemometrics in Analytical Chemistry, Science Press, Perking, 2004, p. 174.

[15] S. Wold, H. Martens, H. Wold, in: A. Ruhe, B. Kågström (Eds.), Proceedings on the Conference on Matrix Pencils, Lecture Notes in Mathematics, Springer-Verlag, Heidelberg, 1983, pp. 286–293.

[16] Z. Rezae, B. Hemmateenejad, S. Khabnadideh, M. Gorgin, Talanta 65 (2005) 21.

[17] G. Jahanbakhsh, N. Ali, Talanta 65 (2005) 1168.

[18] L. Heila, D.E. Mohammadi, Y. yamini, R.G. Brereton, Talanta 62 (2004) 185.

[19] A. Espinosa-Mansilla, A.M. De la Peña, D.G. Gómez, F. Salinas, Anal. Chim. Acta 531 (2005) 257.

[20] I. Merás, T. Díaz, M. Franco, Talanta 65 (2005) 7.

[21] A. Espinosa-Mansilla, A.M. De la Peña, F. Salinas, D.G. Gómez, Talanta 62 (2004) 853.

[22] J. Moros, F.A. Inon, S. Garrigues, M. De la Guardia, Anal. Chim. Acta 538 (2005) 181.

[23] S. Armenta, S. Garrigues, M. de la Guardia, Talanta 65 (2005) 971.

[24] R.S. Freire, M.M.C. Ferreira, N. Durán, L.T. Kubota, Anal. Chim. Acta 485 (2003) 263.

[25] P. Campíns-Falcó, L.A. Tortajada-Genaro, S. Meseguer-Lloret, F. Bosch-Reig, Anal. Bional. Chem. 374 (2002) 1223.

[26] B. Li, D. Wang, C. Xu, Z. Zhang, Microchim. Acta 149 (2005) 205.

[27] C. Lu, J. Lin, C.W. Huie, M. Yamada, Anal. Sci. 19 (2003) 557.

[28] T. Kamidate, A. Ishikawa, T. Segawa, H. Watanabe, Chem. Lett. 23 (1994) 1123.

[29] W.R. Seitz, W.W. Suydam, D.M. Hercules, Anal. Chem. 44 (1972) 957.

[30] G. Mernyi, J.S. Lind, J. Am. Chem. Soc. 102 (1980) 582.

[31] Z.H. Lan, H.A. Mottola, Anal. Chim. Acta 239 (1994) 139.

[32] W. Qin, Z. Zhang, B. Li, S. Liu, Anal. Chim. Acta 372 (1998) 357.

[33] D.M. Haaland, E.V. Thomas, Anal. Chem. 60 (1998) 1193.

[34] A. MacDonal, T.A. Nieman, Anal. Chem. 57 (1985) 936.

[35] Z. Zhang, J. Lv, Huaxue Shiji 9 (3) (1987) 149.