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SPECTROPHOTOMETRIC DETERMINATION OF Ni^{2+}, Co^{3+}, Fe^{2+}, Cu^{2+} CONCENTRATIONS WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL IN AQUEOUS-MICELLAR MEDIUM BASED ON TWO INTENSIVE PARAMETERS

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Abstract. Results comparison was performed within the terms of multi-component analysis for light absorption arrays processed using the method of consecutive separation of graduation surface (MCSGS), developed by the authors, with other methods of pseudo-one-dimensional processing. Determination of Ni^{2+}, Co^{3+}, Fe^{2+}, Cu^{2+} ion concentrations with 1-(2-pyridylazo)-2-naphthol in aqueous-micellar medium on two-dimensional absorption spectra of wave length by pH coordinates were performed. The results of calculation were compared with calculations by least squares method (LSM), partial least squares method (PLS) and principal component regression analysis (PCA).

Keywords: secondary spectrum, 1-(2-pyridylazo)-2-naphthol, complex, simultaneous determination.

1. Introduction

Simultaneous determinations of several components concentrations using overlapped spectra are traditionally applied in spectrophotometry and other non-selective methods of analysis. There are a lot of different methods of processing total analytical signals spectra. They include: the least squares method, partial least squares, principal component analysis, rank annihilation factor analysis (RAFA) and several others.

Articles [1-14] are devoted to simultaneous determination of components by PLS. This calculation method is used for determination of two [1-4], three [5-8], four [9-10] and five [11] components in the co-presence and using multiple methods [12-14].

The method of simultaneous spectrophotometric determination of Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} based on formation of their complexes with 1,5-bis(di-2-pyridyl-methylen)thiocarbonohydrazide (DPTH) is suggested in this paper [15]. Chemometric approaches (PLS and PCA) were applied for extraction of these ions from four-component mixtures. In general, PLS provides the best results. Determination of five component system containing Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+} and Fe^{2+} with substitution of metal-nitrilotriacetic complex (M-NTA) for 4-(2-pyridylazo)-resorcin (PAR) has been described in the article [11]; spectral data were processed by PLS and PCA methods.

Metal ions, such as Co^{2+}, Ni^{2+}, Cu^{2+}, Fe^{3+} and Cr^{3+}, present in electroplating baths in high concentrations, have been simultaneously analyzed by spectrophotometric method with ethylene diamine tetraacetate (EDTA) as a chromogenic reagent [16]. Using this data set, calibrated models have been built based on different chemometric methods.

PLS algorithm, using OSC (orthogonal signal correction), is commonly used for simultaneous determination [17] of cobalt, copper, and nickel; iron, nickel, and cobalt based on creation of their complexes with 1-(2-pyridylazo)-2-naphtol (PAN) in micellar medium [18], by using PLS with direct orthogonal signal correction (DOSC). Linear range is within 0.30–4.50 mg/ml^{-1} for Co^{2+}, 0.20–3.00 mg/ml^{-1} for Ni^{2+}, and 0.30–5.00 mg/ml^{-1} for Fe^{2+}; and for cobalt, nickel, and palladium with 1-(2-pyridylazo)-2-naphtol (PAN) in Tween-80 micellar medium based on singular value decomposition (SVD) [19]. Aqueous micellar medium is used in a lot of works in connection with surface-active substances [18-21].

RAFA method has been offered in the work [22]. Lately, RAFA method has been applied for determination of component concentrations under determination of acidity constants of dibasic acids [23], under spect-

rophotometric determination of equilibrium complexation constants [24], under determination of protonacids using epy acid-base titration [25], by epy kinetic-spectrophotometric method [26]. A new spectrophotometric method has been developed in [27] to determine melamine in milk.

The purpose of the present work is to compare the results of processing two-dimensional absorption spectra for Ni^{2+}, Co^{3+}, Fe^{2+}, Cu^{2+} ions in the form of complexes with PAN in aqueous-micellar medium in the mixtures by epy proposed method of consecutive separation of "graduated surface" (MCSGS) in the "mixture surface" with other methods.

An algorithm for determination of ion concentrations from the spectra on two-dimensional dependence was proposed in the paper [28]. Essential condition is the presence of independent parameter area where spectral overlapping and interference of other mixture components are absent. It allows the most accurate separation of component spectrum from the general matrix of the mixture with minimal errors. The separation of complex spectra of individual ions according to their output dependencies from pH has been performed in the work [29]. This work offers the method of separating a spectrum based on two intensive parameters.

2. Experimental

2.1. Reagents

Metal ions standard solutions (0.01 mol/dm^3) were prepared by dissolving metal weight of extra purity in the nitric acid.

1-(2-pyridylazo)-2-naphthol (produced by "Reanal" company) was additionally purified by recrystallization from the isopropyl alcohol. Working solution (concentration: $4 \cdot 10^{-3}$ mol/dm^3) was prepared by dissolving necessary PAN sample in ethanol and diluting to the scale in a volumetric flask.

The SAS (surface-active substance) solution – sodium ethoxydodecylsulphate with the average molar weight of 376 g/mol LES-ME 70 (initial substance is gel with a mass fraction of the basic substance of 70.1 %, manufacturer: "Texapon", No. 70) was prepared with a mass fraction ω = 15 % by dissolving a weigh in the bidistilled water.

Standard phthalate buffer solution, pH = 4, was prepared by mixing 0.1 mol/dm^3 hydrochloric acid solution with 0.2 mol/dm^3 potassium hydrogenphtalate with 1:4 ratio.

Standard borate buffer solution, pH = 9.2, was prepared by dissolving 19.07 g of $Na_2B_4O_7 \cdot 10H_2O$ in the bidistilled water and transferring quantitively in 1000 cm^3 volumetric flask, diluting to the scale with the bidistilled water.

2.2. Obtaining Two-Dimensional Spectra

Complex absorption spectra and their outcome depending on pH were measured on a spectrophotometer-ionometer (SF-46 LOMO spectrophotometer, St. Petersburg, Russia; in quartz cells (l = 1 cm) and pH meter (pH-meter 150 MI universal ionometer, Moscow, Russia; with ESKL-08M combined laboratory glass electrode and TDL-1000 temperature sensor) with pH-electrodes in a cell (Fig. 1). The titrant (HCl, 0.55 mol/dm^3) was moved through a flexible capillary from the microburette into a cell. After each step of titrant addition and stirring, pH and absorbance measurements in λ = 520–800 nm range were carried out with 10 nm increments which are enough for getting absorption values and providing necessary accuracy of determining metal ions. These measurements were done for the solution containing metal cations as well as for comparison solution. After subtraction, the two-dimensional ion-complex absorption spectrum with PAN according to λ and pH was acquired.

2.3. Procedure

2 cm^3 of model mixture was sampled. Concentration of every metal in the sample should not exceed $c(Me^{z+})$ = = $1 \cdot 10^{-4}$ mol/dm^3. 1 cm^3 of ascorbic acid (mass fraction is 10 %) is added to the aliquot sample allowing 2–3 min for the reaction to complete. Then 1.5 cm^3 of 1-(2-pyridylazo)-2-naphtol, 10 cm^3 of biphthalate buffer solution with pH = 4.01 and 2.5 cm^3 of sodium sulfoethoxylate (mass fraction is 15 %) are also added to the sample. The mixture is after that transferred to 25 cm^3 volumetric flask and diluted to scale with bidistilled water. Aliquot (8 cm^3) of is placed in 1cm-width cell and titrated by the hydrochloric acid in 0.1 cm^3 increments measuring absorbance and pH of the solution in λ = 520–800 nm range.

Calculations were carried out in Matlab 6.5 software. The measured arrays of values $A(i, j)$ were adjusted to reflect changes in the solution volume, $A^{cor}(i,j)$, according to the Eq. (1). Titration provided pH values that were irregularly split on the scale. During titration, different pH values were received for different mixture proportions. To compare the results and estimate methods quality, all spectra were brought to a single scale λ–pH. For this purpose the spectra were subjected to a cubic spline approximation. Value $A^{(0)}$ (n_λ, n_{pH}) was calculated for pH_i = 4.0–0.5i (i = 0–n_{pH}) where n_{pH} is the number of pH values, and i takes the values within 0–7 allowing thus for pH values within the range from 0.5 to 4.0.

$$A^{cor}(i, j) = A(i, j) \cdot (V_0 + \Delta V_j)/V_0 \qquad (1)$$

where V_0 = 8.0 cm^3 − aliquot volume of complexes solution; ΔV_j − the volume of HCl added to V_0 during the titration.
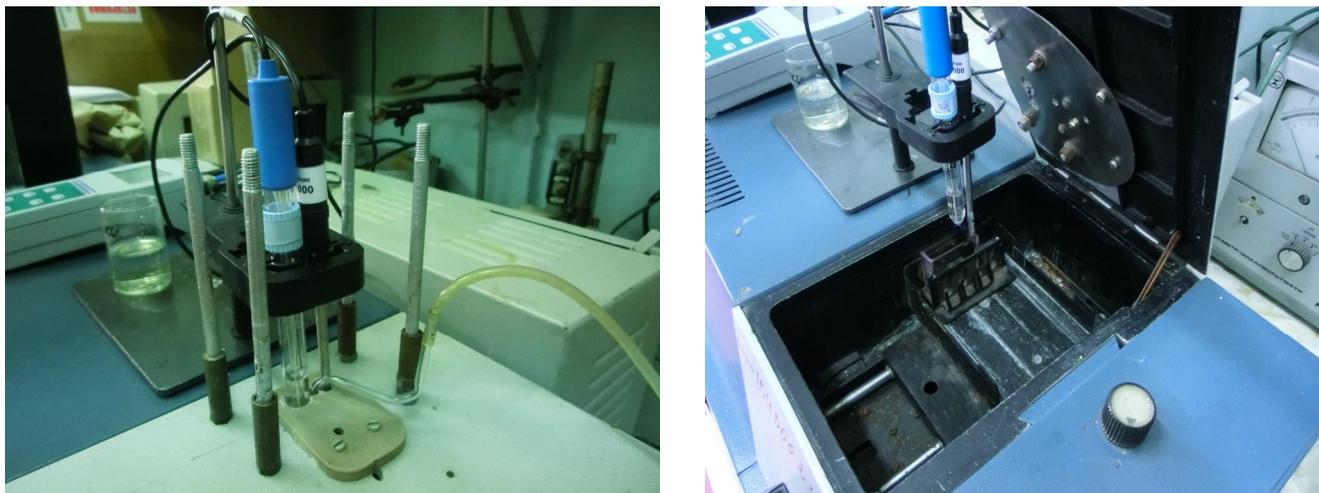
Fig. 1. Photos of spectrophotometer-ionometer

2.4. Data Processing

Using found $\left(c_j^{det}\right)$ and given $\left(c_j^{input}\right)$ component concentrations, root-mean-square deviations from the given concentrations have been estimated.

$$s_c = \sqrt{\frac{\sum_{j=1}^{n}\left(c_j^{det} - c_j^{input}\right)^2}{n-1}} \qquad (2)$$

where n is the number of parallel determinations of component concentration for a certain mixture. Three simultaneous studies were carried out for every mixture and for individual solutions.

The method is applied directly to two-dimensional spectra at factorization of $E(n_1, n_2)$ calibration matrix on the product of two vectors [28]. Two-dimensional calibration matrix E (pure component two-dimensional absorption spectrum) of l-pH coordinates breaks up in two vectors:

$$E(n_\lambda, n_{pH}) = V(n_\lambda, l) \cdot Q(l, n_{pH}) \qquad (3)$$

where n_l – the wave length number in two-dimensional spectrum; n_{pH} – the number of pH values in which absorption coefficients were measured; V – the vector-spectrum of identifiable ion complex with PAN at pH of maximum emerge; Q – the complex emerge vector according to pH.

Components concentration is calculated by the following Eq. (4):

$$c = V^+ \cdot A^{(0)} \cdot (Q^+)^T \qquad (4)$$

where $A^{(0)}$ – the matrix of initial light absorption in the analyzed system, $(^+)$ – indicates the matrix pseudoinversion $(V^+ = (V^T \cdot V)^{-1} \cdot V^T)$. Thus we assume that the light absorption of the mixture is completely defined by a single component.

However at such calculation the result will be correct only if $A^{(0)}$ contains a two-dimensional spectrum of a single determinate component. In a multi-component system analysis, determined concentrations are distorted by the presence of other absorptive components. In order to bring test results closer to the actual values we offer to use the step-by-step approach (iteration method).

After estimating concentration by the Eq. (4), restoration of the response surface is carried out by the following Eq. (5).

$$A1 = V \cdot Q \cdot c \qquad (5)$$

There are areas on λ–pH surface where the mixture absorption corresponds only to one component. In this point other components have either zero pH output or zero light absorption. $A1$ surface in these areas lies over $A^{(0)}$, and on the last surface we observe $A1(i, j) < A(i, j)$. After element replacements under the following condition:

if $A(i, j) - A1(i, j) > 0.001$ then $A^{(1)}(i, j) = A1(i, j)$, calculation by the Eq. (4) is carried out $c^{(1)} = V^+ A^{(1)} \cdot (Q^+)^T$

After k step-by-step approaches, the result of $c^{(k)}$ does not change. $^{(1)\,(2)\dots(k)}$ are iteration numbers.

The second component concentration is calculated out of the difference matrix $DA^{(0)} = A^{(0)} - A^{(k)}$ using the same algorithm. For the third component of the system, the difference matrix $DDA^{(0)} = DA^{(0)} - DA^{(k)}$ is used.

3. Results and Discussion

Absorption spectra overlap fully only for Ni²⁺ and Cu²⁺ ion complexes among the studied Ni²⁺, Co³⁺, Fe²⁺, Cu²⁺ ion complexes with PAN in aqueous-micellar medium. Absorption spectra for Co³⁺ and Fe²⁺ ion

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complexes overlap partially (Fig. 1). Maximum errors appear during the determination of Ni^{2+} and Cu^{2+} ion complexes concentrations under simultaneous determination of the mentioned above complexes using component extinctions at different wave lengths.
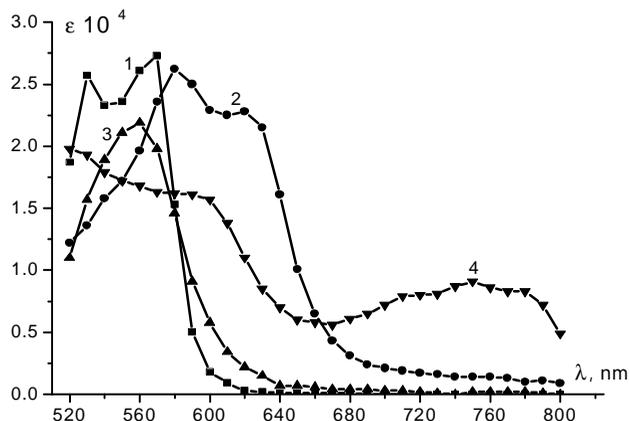
Fig. 1. Absorption spectra of $Ni(PAN)_2$ (1), $Co(PAN)_3$ (2), $Cu(PAN)^+$ (3) and $Fe(PAN)_2$ (4) ion complexes with 1-(2-pyridylazo)-2-naphtol in acid medium at pH = 4. Mass fraction (ω) of sodium ethoxydodecylsulphate is 1.5 %
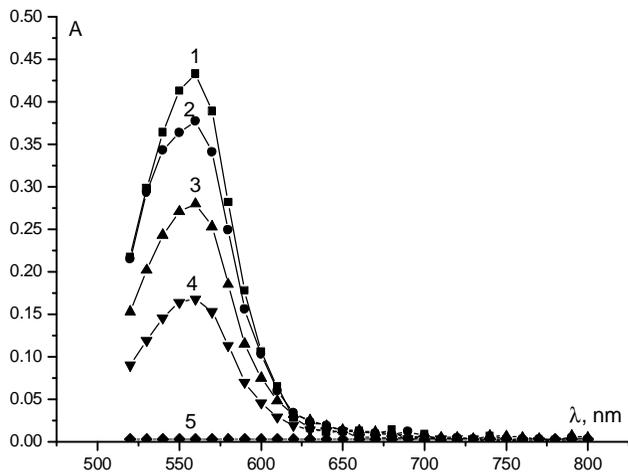
Fig. 2. Modification of Cu^{2+} ion complex with 1-(2-pyridylazo)-2-naphtol absorption spectra during titration; pH: 3.96 (1); 2.08 (2); 1.56 (3); 1.16 (4) and 0.8 (5)

As we can see, $Fe(PAN)_2$ complex has more long-wave absorbance. It is reasonable to determine it first. The next in absorbance maximum displacement is $Co(PAN)_3$ complex; it is to be determined second. $Ni(PAN)_2$ and $Cu(PAN)_2$ complexes are more difficult to determine because of the similarity of their absorption spectra. During titration of complexes, some of them are destroyed (Ni^{2+}, Cu^{2+}), other are not (Co^{3+}, Fe^{2+}). Fig. 2 shows one example of $Cu(PAN)_2$ the complex spectra at various pH values.

Fig. 3 shows the spectra of cobalt and copper mixture. The initial spectrum consists of completely overlapped cobalt and copper complex spectra preventing

from determining the concentrations of metal in the mixture. During titration, the mixture spectrum modification is observed resulting from the destruction of copper complex. Therefore, the amount of information during titration is increased as a result of obtaining spectra sets that differ greatly from one another. It allows to calculate concentrations of metal complexes in the mixture.
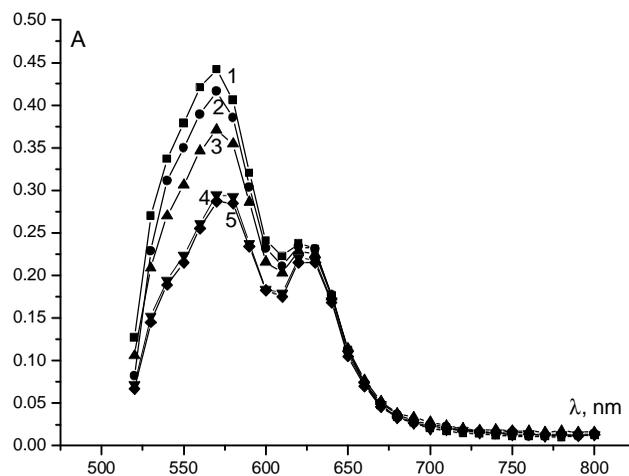
Fig. 3. Modification of Cu^{2+} and Co^{3+} ion complexes mixture with 1-(2-pyridylazo)-2-naphtol absorption spectra during titration; pH: 3.96 (1); 2.08 (2); 1.56 (3); 1.16 (4) and 0.8 (5)

Table 1 and 2 show calculations of two- and three-component mixtures of metal ion complexes in the form of complexes with PAN.

As we can see, in two-component systems, LSM is not inferior to the proposed calculation algorithm in terms of accuracy.

In a three-component system, the number of determination errors by MCSGS is several times smaller than the number of determination errors by LSM. Pseudo one-dimensional method of determining three components is marked by unsatisfactory errors.

The value of determined errors grows in the system with the increase of ion number. Calculations using the method of consecutive separation of graduation surface show more concentration errors both for two-component and three-component systems in the Fe^{2+}, Co^{3+}, Ni^{2+}, Cu^{2+} row which corresponds to sequence determination.

An attempt to determine and calculate a four-component system didn't bring necessary results because of the neighbored overlapped spectra and similar pH output dependencies for $Ni(PAN)_2$ and $Cu(PAN)_2$ complexes. So it was decided to test combination of interligand exchange and spectrophotometric titration. Differences in the interreactions of metal complexes with PAN and 8-hydroxyquinoline in aqueous-miccelar medium at pH = 9.18 are used in the work [29]. It was shown that metal ion complexes with PAN are destroyed completely resulting in formation of the complex with 8-hydroxy-quinoline, absorbed in other spectral area. This is Cu^{2+} ion.

Table 1

Calculations of two-component model mixtures obtained by the developed MCSGS algorithm and using LSM, PCA, and PLS methods

	Added C, 10^{-5} mol/dm³	Obtained MCSGS C, (S_c) 10^{-5} mol/dm³	Obtained LSM C, (S_c) 10^{-5} mol/dm³	Obtained PCA C, (S_c) 10^{-5} mol/dm³	Obtained PLS C, (S_c) 10^{-5} mol/dm³
Ni^{2+}	1.21	1.06 (0.11)	1.08 (0.06)	1.19 (0.11)	1.19 (0.02)
Co^{3+}	1.22	1.21 (0.001)	1.13 (0.07)	1.75 (0.11)	1.01 (0.09)
Ni^{2+}	1.21	1.21 (0.001)	1.11 (0.07)	1.39 (0.11)	0.93 (0.19)
Fe^{2+}	1.22	1.20 (0.012)	1.16 (0.04)	1.42 (0.11)	0.76 (0.33)
Fe^{2+}	1.22	1.20 (0.04)	0.92 (0.21)	1.87 (0.11)	1.01 (0.15)
Co^{3+}	1.22	1.18 (0.03)	1.13 (0.07)	2.06 (0.11)	0.96 (0.19)
Ni^{2+}	1.21	1.21 (0.00)	1.04 (0.12)	1.57 (0.25)	1.55 (0.24)
Cu^{2+}	1.17	0.65 (0.37)	1.16 (0.01)	0.91 (0.18)	0.60 (0.41)
Co^{3+}	1.22	1.22 (0.001)	0.89 (0.23)	0.72 (0.35)	0.95 (0.19)
Cu^{2+}	1.17	0.63 (0.38)	1.08 (0.06)	0.71 (0.33)	0.99 (0.13)
Fe^{2+}	1.22	1.20 (0.012)	0.92 (0.21)	0.55 (0.47)	1.23 (0.01)
Cu^{2+}	1.17	1.04 (0.095)	1.05 (0.08)	0.53 (0.45)	0.42 (0.53)

Table 2

Calculations of three-component model mixtures obtained by the developed MCSGS algorithm and LSM, PCA, and PLS methods

	Added C, 10^{-5} mol/dm³	Obtained MCSGS C, (S_c) 10^{-5} mol/dm³	Obtained LSM C, (S_c) 10^{-5} mol/dm³	Obtained PCA C, (S_c) 10^{-5} mol/dm³	Obtained PLS C, (S_c) 10^{-5} mol/dm³
Ni^{2+}	0.81	0.62 (0.13)	0.60 (0.14)	1.07 (0.19)	1.35 (0.39)
Fe^{2+}	0.81	0.81 (0.005)	0.81 (0.002)	0.79 (0.02)	0.14 (0.48)
Co^{3+}	0.81	0.77 (0.03)	0.66 (0.11)	0.51 (0.22)	0.44 (0.26)
Ni^{2+}	0.81	0.697 (0.07)	0.63 (0.12)	0.56 (0.17)	1.06 (0.18)
Fe^{2+}	0.81	0.81 (0.00)	0.35 (0.33)	0.72 (0.07)	0.009 (0.57)
Cu^{2+}	0.81	0.51 (0.195)	0.61 (0.12)	0.77 (0.01)	0.53 (0.18)
Ni^{2+}	0.81	0.33 (0.33)	0.30 (0.35)	0.41 (0.28)	0.62 (0.13)
Co^{3+}	0.81	0.81 (0.00)	0.82 (0.003)	0.86 (0.03)	0.84 (0.02)
Cu^{2+}	0.81	0.85 (0.05)	0.69 (0.07)	0.74 (0.03)	0.47 (0.22)
Fe^{2+}	0.81	0.81 (0.00)	0.59 (0.16)	0.02 (0.43)	1.09 (0.19)
Co^{3+}	0.81	0.79 (0.02)	0.75 (0.04)	1.35 (0.38)	0.71 (0.08)
Cu^{2+}	0.81	0.52 (0.19)	0.64 (0.09)	0.17 (0.43)	0.16 (0.44)

Table 3

Results of the determination in four-component model mixtures obtained by the worked out algorithm (MCSGS) and PLS method

	Ni^{2+}	Fe^{2+}	Co^{3+}	Cu^{2+}
Added, C, 10^{-5} mol/dm³	**0.80**	**0.81**	**0.81**	**0.78**
Found by MCSGS C, 10^{-5} mol/dm³	0.59	0.81	0.74	0.68
Found by PLS C, 10^{-5} mol/dm³	0.14	0.95	1.28	0.33
Errors of MCSGS, S_c	0.15	0.00	0.05	0.07
Errors of PLS, S_c	0.47	0.09	0.33	0.32

Table 4

Results of concentrations determination of Ni²⁺, Co³⁺, Fe²⁺, Cu²⁺ in the mineral water

Subject	Added, mg/kg				Found, mg/kg			
	Co^{2+}	Ni^{2+}	Cu^{2+}	Fe^{2+}	Co^{3+}	Ni^{2+}	Cu^{2+}	Fe^{2+}
Mineral water	-	-	-	-	-	0.30	8.00	14.20
	13.00	12.00	5.00	7.00	12.40	12.90	13.50	22.10
S_c			-		0.40	0.49	0.72	0.28

Thus it was decided to try the microtitration method of four-component system with 8-hydroxyl-quinoline to remove copper ions from the system with the following spectrophotometric microtitration in three-component system now. Table 3 shows results of ion determination in the four-component system by the example of model mixtures.

Table 4 shows one example of Ni^{2+}, Co^{3+}, Fe^{2+}, Cu^{2+} concentration determination in the mineral water using the developed calculation algorithm. Water sample was evaporated to obtain tenfold concentrate. 2 cm^3 of obtained solution was analysed. Analysis was performed according to the procedure described above. The accuracy of the analysis was verified by the standard addition method.

4. Conclusions

1. The results of simultaneous determination of Ni^{2+}, Co^{3+}, Fe^{2+}, Cu^{2+} ion complexes with PAN in the aqueous-micellar medium on two-dimensional dependence of the wave length and pH by the proposed method of consecutive separation of graduation surface in the mixture surface were compared with other methods and with the results of LSM.

2. Combination of interligand exchange with the spectrophotometric micro-titration allows to determine ions of Fe^{2+}, Co^{3+}, Ni^{2+}, Cu^{2+} as complexes with PAN in four-component model mixtures with minimal errors.

Abbreviations list

MCSGS – Method of consecutive separation of graduation surface
LSM – Least squares method
PCA – Principal component analysis
PLS – Partial least squares
RAFA – Rank annihilation factor analysis
PAN – 1-(2-pyridylazo)-2-naphtol
SAS – Surface-active substance

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**СПЕКТРОФОТОМЕТРИЧНЕ ВИЗНАЧЕННЯ
КОНЦЕНТРАЦІЙ Ni^{2+}, Co^{3+}, Fe^{2+}, Cu^{2+}
З 1-(2-ПІРИДИЛАЗО)-2-НАФТОЛОМ У ВОДНО-
МІЦЕЛЯРНОМУ СЕРЕДОВИЩІ ЗАЛЕЖНО ВІД
ДВОХ ІНТЕНСИВНИХ ПАРАМЕТРІВ**

Анотація. *У межах багатокомпонентного аналізу проведено співставлення результатів оброблення масивів світлопоглинання методом почергового вписування градуювальної поверхні (МПВГП), розробленим авторами, з іншими методами псевдоодномірного оброблення. Проведено визначення Ni^{2+}, Co^{3+}, Fe^{2+}, Cu^{2+} з 1-(2-піридилазо)-2-нафтолом у водно-міцелярному середовищі за двовимірними спектрами поглинання в координатах довжина хвилі – pH. Розрахунки порівняні з розрахунками за методом найменших квадратів (МНК), парціальних найменших квадратів (МПНК) і методу головних компонентів регресії (МГК).*

Ключові слова: спектр другого порядку, 1-(2-піридилазо)-2-нафтол, комплекс, одночасне визначення.