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THE DETERMINATION OF CONCENTRATIONS OF IONS Zn^{2+}, Cd^{2+}, Mn^{2+} WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL IN AQUEOUS-MICELLAR MEDIUM ON TWO-DIMENSIONAL ABSORPTION SPECTRA OF WAVE LENGTH BY pH COORDINATES

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ABSTRACT. An iterative author's algorithm (step-by-step approach) for determine concentrations of ions Zn^{2+}, Cd^{2+}, Mn^{2+} with 1-(2-pyridylazo)-2-naphthol in aqueous-micellar medium on two-dimensional spectra of absorption of wave length by pH coordinates is proposed. Different two- and three-component model mixtures analyses were carried out. Test results comparison of determination and roof-mean-square deviation from introduced concentrations by proposed iterative algorithm and least squares method shows advantages of iterative algorithm for three-component systems and congruent accuracy for two-component systems.

Keywords**:** *two-dimensional absorption spectra, consistent method of incorporating surface, least squares method, 1-(2-pyridylazo)-2-naphthol, complexes, determination of ions Zn^{2+}, Cd^{2+}, Mn^{2+}*

INTRODUCTION

Using of the two-dimensional spectra and spectra of high order in the chemical analysis increases amount of information about the system and increases accuracy as compared with one dimension spectra and scalar measurements. Spectrophotometric method is simple and cheap as compared with instrumental methods of atomic spectroscopy. Two-dimensional spectra of multicomponent systems create additional abilities for the determination of several components in the system. Coordinate pH can be complementary coordinate to λ. Two-dimensional spectra can be handled using known methods.

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RAFA method assumes calibration matrix decomposition to the product of two vectors and usage of them for the calculation of the concentrations. Such calculations are overlaid with systematic errors, which arise from the interference of the components. Developed algorithm allows to negate systematic errors.

Two- and three-component zinc-cadmium-manganese subsystems occur in the analysis of special aluminum alloys, in waste waters of galvanizing plants, in the analysis of vegetable agricultural products.

Spectrophotometric determination of Zn^{2+} and Cd^{2+} ions at joint presence in waste waters using chelates extraction with PAN in chloroform is described in [1]. It is also specified that owing to the similarity of absorption spectra complexes with PAN, the determination errors are great and yield to dithizone determinations.

In [2] there is shown the possibility of determination of Zn^{2+} and Cd^{2+} ions with PAN in aqueous-micellar medium on two-dimensional spectra of wave length by pH with formation of a pseudo-one-dimensional vector-spectrum.

Rank annihilation factor analysis (RAFA) method was offered, proved and developed in the works [3, 4]. RAFA method was created for processing of two-dimensional spectra. Last years RAFA method is used for the determination of the concentration of the component at determination of equilibriums constants [5], at spectrophotometric determination of the constants of acidity of dyes [6], at the determination of the protonacids by the acid-base titration method [7], the kinetic - spectrophotometric analysis [8]. A new spectrophotometric method has been developed in [9] to determine melamine in milk. The RAFA method is applied at the determination of one component in the presence of other components showing an analytical signal in the same intensive parameter space [10-12]

The purpose of the present work is to study the possibilities of consistent method of incorporating surface at step-by-step determination of Zn^{2+}, Cd^{2+}, Mn^{2+} ions out of two-dimensional absorption spectra of complexes with PAN of λ-pH coordinates in two- and three - component systems.

RESULTS AND DISCUSSION

Optimization of spectrum measurements of wavelength and pH

Absorption spectra of Zn^{2+}, Cd^{2+} and Mn^{2+} ion complexes with the PAN in aqueous-micellar solutions remain quite similar (fig. 1). Simultaneous determination using component extinctions at different wave lengths is meaningless.

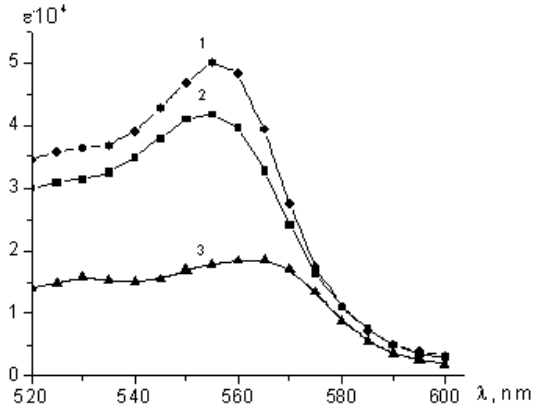

Figure 1. Absorption spectra of $Zn(PAN)_2$ (1), $Cd(PAN)_2$ (2), $Mn(PAN)_2$ (3) complexes in the aqueous-micellar medium. Mass fraction of sodium ethoxydodecylsulphate ω = 2,5 %. Ion concentrations $c(Zn(PAN)_2)$= 0,1-1·10^{-5} mol/l, $c(Cd(PAN)_2)$= 0,1-1·10^{-5} mol/l, $c(Mn(PAN)_2)$= 0,1-1·10^{-5} mol/l

If pH is used as an intensive parameter of analytical signal, additional differences in absorption coefficients ($\varepsilon_{\lambda,pH,j}$) of components are shown.

$$\varepsilon_{\lambda,pH,j} = \varepsilon_{\lambda.j}\alpha_{pH,j} \quad (1)$$

The ($\alpha_{pH,j}$) yield of complexes - pH relationships are presented in fig. 2.

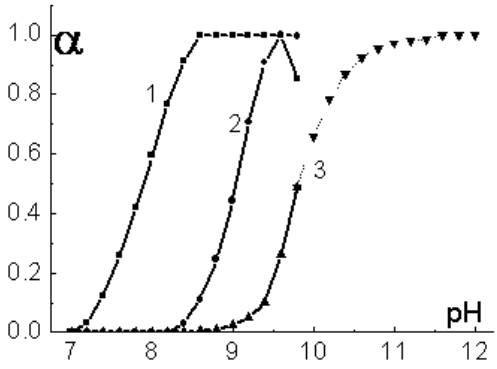

Figure 2. The yield of complexes - pH relationship in aqueous-micellar medium $Zn(PAN)_2$ (1), $Cd(PAN)_2$ (2), $Mn(PAN)_2$ (3). ω(sodium ethoxydodecylsulphate) = 2,5 %. Ion concentrations $c(Zn(PAN)_2)$ = 0,1-1·10^{-5} mol/l, $c(Cd(PAN)_2)$ = 0,1-1·10^{-5} mol/l , $c(Mn(PAN)_2)$ = 0,1-1·10^{-5} mol/l

For the subsequent calculations absorption spectra of each complex at different pH were normalized A_i/A_{max}, and after overlapping, there were selected wave length ranges in which spectrum structure is similar. This range is λ= 530-570 nm.

The result of the successive approximations for $Zn(PAN)_2$ according to the pH at λ = 555 nm is shown on the fig. 3. As it seen from the fig. 3, twenty successive approximations stabilize $c(Zn^{2+})$ value.

Beer's law holds in the whole pH range used

The yield of the complexes according to the pH is described by the equation of mass action law: $[M(PAN)_2] = \beta [M^{2+}] [HPAN] 10^{2pH}$. In order to keep complex yield portion constant (or close to constant) it is necessary for the reagent concentration in the solution to be considerably (10 times and more) higher than metal cation concentration, [HPAN] >> $[M^{2+}]$. In spite of the taken measures, it should be noted that after subtracting the first inscribed surface from the measured, all accumulated differences in the yield of the first complex -pH relationships remain in the residual surface. An attempt to exclude accumulation of distortions before calculating concentration of the second component by singular decomposition of difference matrix $DA^{(0)}$ by means of the "svd" [4] software and restoration using two eigenvalues didn't show any positive results. Cadmium concentrations do not vary significantly. The absence of the significant distortions in the residual analytical signal of spectra, especially at lower pH, is due to fulfillment of the following condition: $\beta_2/\beta_1 > \beta_1$.

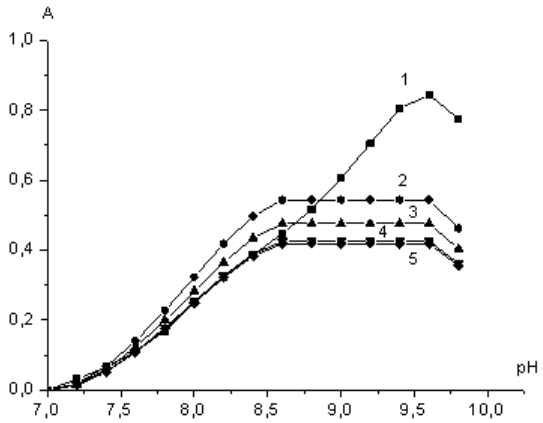

Figure 3. Relationships: 1 – total light absorbance of the mixture according- pH at λ = 555 nm; 2,3,4,5 – restored light absorbance at λ = 555 nm after one, three, fifteen and twenty iterations.

Analysis of the model solutions

Simultaneously determination of ion concentrations (c_j) for pseudo-one-dimensional spectra $\mathbf{A}(n_\lambda + n_{pH},1)$ was conducted by solving combined equations of the (7) type according to the least squares method.

$$\mathbf{E}(n_\lambda + n_{pH}, m)\cdot\mathbf{c}(m, 1) = \mathbf{A}(n_\lambda + n_{pH}, 1) \quad (2)$$

$$\mathbf{c} = (\mathbf{E}^{\mathbf{T}}\cdot\mathbf{E})^{-1}\cdot\mathbf{E}^{\mathbf{T}}\cdot\mathbf{A} \quad (3)$$

$\mathbf{E}(n_\lambda + n_{pH}, m)$ – matrix of the molar absorption coefficients has $n_\lambda + n_{pH}$ lines and m columns; m – number of components; $\mathbf{E}^{\mathbf{T}}$ – transpose of the matrix of coefficients.

The results of ion determination in the model solutions are presented in Table 1. Using found (c_j^{det}) and given (c_j^{input}) component concentrations, root-mean-square deviations from the given concentrations have been estimated.

$$s_c = \sqrt{\frac{\sum_{j=1}^{n}(c_j^{\det} - c_j^{input})^2}{n-1}} \quad (4),$$

where n – the number of three-component mixtures, or the number of two-component mixtures in which j-component is present. Such estimated deviation includes both random and systematic errors of the determination and acts as a measure of reproducibility.

Table 1. The results of ion concentrations determination in the model mixtures by iterative author's algorithm (IAA) and least squares method (LSM)

No	Analytical concentration, C 10^5 (mol L^{-1})			Found concentration, C,S_c 10^5 (mol L^{-1})			
	$Zn(PAN)_2$	$Cd(PAN)_2$	$Mn(PAN)_2$	Used method	$Zn(PAN)_2$	$Cd(PAN)_2$	$Mn(PAN)_2$
1	0.80	0.80	0.80	IAA	0.81	0.94	0.69
				LSM	1.27	0.35	0.18
2	1.20	0.40	0.40	IAA	1.10	0.49	0.21
				LSM	1.12	0.62	0.05
3	0.40	0.40	1.20	IAA	0.44	0.51	0.73
				LSM	0.47	0.40	1.58
4	0.40	1.20	0.40	IAA	0.46	1.04	0.33
				LSM	0.54	0.89	0.17
				IAA, S_c	0.06	0.13	0.18
				LSM, S_c	0.27	0.30	0.49

No	Analytical concentration, C 10^5 (mol L^{-1})			Found concentration, C,S_c 10^5 (mol L^{-1})			
	$Zn(PAN)_2$	$Cd(PAN)_2$	$Mn(PAN)_2$	Used method	$Zn(PAN)_2$	$Cd(PAN)_2$	$Mn(PAN)_2$
5	0.50	2.00	-	IAA	0.46	2.10	-
				LSM	0.46	1.99	-
6	0.50	-	2.00	IAA	0.48	-	2.23
				LSM	0.56	-	1.88
7	-	1.00	1.00	IAA	-	0.98	1.12
				LSM	-	0.81	1.10
8	-	2.00	0.50	IAA	-	2.10	0.45
				LSM	-	1.91	0.57
9	1.00	-	1.00	IAA	1.08	-	0.95
				LSM	0.89	-	1.15
				IAA, S_c	0.06	0.10	0.16
				LSM, S_c	0.09	0.11	0.12

Sequential determinations by developed method measure first from three components more accurately, then they measure second and worst accurately they measure third component. The result of the determination of first determined component Zn^{2+} is almost five times accurately then the result on LSM. There are the advantages for other ion but they are less. In spite of the errors given in the table, developed method results in the higher accuracy compared to the simultaneous determination using LSM.

As it seen from the results of analysis, working range for such determinations for three ions is $(0,2\text{-}2,0)\cdot10^{-5}$ mol·L^{-1}. Fewer concentrations have greater relative error.

Determination of Zn^{2+} and Mn^{2+} in oatmeal

The sample of oat «Hercules» TM «Dobrodiya», manufacturer CJSC «Niva», Ukraine, Luhansk city, was analysed. Analysis of oat was performed according to the method: 10 g of accurately weighed portion of oat is incinerated in the muffle furnace for 3 hours at the 740 K and dissolved in the 15 ml of diluted nitric acid. Mixture was filtered into the 50 ml volumetric flask after the dissolution of metal salts. Filtrate was diluted to the volume with water. 2,5 ml of the obtained solution was taken for analysis according to the described method.

For example, Table 2 shows the results of Zn^{2+} and Mn^{2+} determination in oatmeal using consistent method of incorporating surface. The method assumes ignition of the sample, dissolution in HNO_3 deposition and abstraction of Fe^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+} ion complexes with PAN at pH 6,5-7. Neutral water

insoluble chelates Fe^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+} with PAN deposited from an aqueous solution without sodium ethoxydodecylsulphate. Aqueous phase (filtrate) is used to determine Zn^{2+} and Mn^{2+}. Cadmium in vegetable objects cannot be determined by the given procedure, since its concentration significantly smaller. The accuracy of the analysis is verified by the addition technique.

Table 2. Concentration results of Zn^{2+}, Mn^{2+} in oatmeal

№	Added		Found				Concentration in sample	
	m(Zn^{2+}), mg	m(Mn^{2+}), mg	c(Zn^{2+}), mg/kg	*s*(Zn^{2+})	c(Mn^{2+}), mg/kg	s(Mn^{2+})	c(Zn^{2+}), mg/kg	c(Mn^{2+}), mg/kg
1	-	-	15.0 19.4	0.5	93.0 17.0	0.6	15.0	17.0
2	-	-	20.0		17.8		20.0	17.8
3	-	-	19.1		18.2		19.1	19.0
4	13	11	32.4	0.8	30.2	0.9	19.4	19.2
5	13	11	30.9		28.5		17.9	17.5
6	13	11	31.5		29.1		18.5	18.1

The results of the determination of mass fraction for c(Zn^{2+})=18,9 mg/kg, c(Mn^{2+})=18,1 mg/kg. Standard deviation s(Zn^{2+})=1,3 mg/kg, s(Mn^{2+})=0,9 mg/kg, Relative standard deviation S_r(Zn^{2+})=0,07, S_r(Mn^{2+})=0,05, «confidential interval» Δc(Zn^{2+})=1,4 mg/kg, Δc(Mn^{2+})=0,9 mg/kg.

Zinc concentration 19,1 ± 0,7 mg/kg, maximum admissible concentration (MAC) = 27 mg/kg Manganese concentration 18,1 ± 0,9 mg/kg, MAC = 50 mg/kg.

As it seen from the table 1, c_{min} (Cd^{2+}) is $3 \cdot S_c$ is 4 mg/kg, MAC (Cd^{2+}) is 0,1 mg/kg.

V – vector-spectrum of dimensional ion complexes Zn^{2+} and Mn^{2+} with PAN at pH of maximum emerge; **Q** – complex Zn^{2+} and Mn^{2+} emerge vectors according to the pH; $\mathbf{A}^{(0)}$ – the matrix of initial absorption in the analyzed system of oatmeal are presented as an example in the Table 3-5. Weight of the sample was 10,0 g.

Table 3. The molar absorption coefficients of the complexes $Zn^{2+}$and Mn^{2+} with PAN ($\varepsilon \cdot 10^{-2}$ l·mol·cm)

λ, nm	530	535	540	545	550	555	560	565	570
ε_{Zn}	381,7	377,0	401,0	441,0	486,0	519,0	499,0	405,0	280,0
ε_{Mn}	121,0	126,0	124,0	127,0	133,0	137,0	139,0	132,0	112,0

Table 4. Depending of emerge complex $Zn^{2+}$and Mn^{2+} with PAN according to pH.

pH	7.0	7.2	7.4	7.6	7.8	8.0	8.2	8.4	8.6	8.8	9.0	9.2	9.4	9.6	9.8
Q_{Zn}	0	0,034	0,125	0,258	0,420	0,594	0,768	0,914	1	1	1	1	1	1	0,850
Q_{Mn}	0	0	0	0	0	0	0	0	0	0	0,005	0,01	0,025	0,050	0.100

Table 5. The initial absorbances in the analyzed system of oatmeal.

pH λ,nm	7.0	7.2	7.4	7.6	7.8	8.0	8.2	8.4	8.6	8.8	9.0	9.2	9.4	9.6	9.8
530	0	0,032	0,072	0,120	0,170	0,220	0,266	0,306	0,338	0,378	0,399	0,423	0,506	0,532	0,663
535	0	0,030	0,071	0,119	0,169	0,220	0,267	0,307	0,336	0,373	0,393	0,417	0,493	0,529	0,663
540	0	0,031	0,074	0,124	0,178	0,232	0,282	0,324	0,355	0,393	0,414	0,439	0,515	0,557	0,685
545	0	0,035	0,083	0,138	0,198	0,258	0,312	0,358	0,392	0,432	0,456	0,484	0,562	0,604	0,731
550	0	0,039	0,092	0,154	0,220	0,285	0,346	0,396	0,433	0,477	0,503	0,535	0,618	0,658	0,781
555	0	0,042	0,099	0,166	0,236	0,306	0,370	0,423	0,462	0,506	0,535	0,570	0,658	0,697	0,818
560	0	0,0401	0,094	0,157	0,224	0,291	0,351	0,401	0,436	0,479	0,506	0,540	0,627	0,677	0,775
565	0	0,0323	0,075	0,124	0,176	0,228	0,276	0,316	0,346	0,384	0,402	0,426	0,506	0,566	0,695
570	0	0,0208	0,049	0,081	0,115	0,150	0,182	0,209	0,230	0,257	0,265	0,278	0,339	0,400	0,523

CONCLUSIONS

1) When consistent method of incorporating surface is used for determination, in three-component as well as in two-component systems, in the Zn^{2+}, Cd^{2+}, Mn^{2+} row, according to the determination sequence, concentration errors are increasing.

2) In a three-component system, determination errors using consistent method of incorporating surface are several times fewer, than determination errors using LSM. The repeatability of the measurements of Zn^{2+} is 5 times better, but for Cd^{2+} and Mn^{2+} is 2 times better than the results calculated using LSM.

The use of pseudo-one-dimensional method to determine three components shows unsatisfactory errors.

3) In two-component systems, LSM does not yield to the consistent method of incorporating surface by accuracy.

EXPERIMENTAL SECTION

Apparatus and software

All absorbance measurements were obtained using a spectrophotometer (spectrophotometer SF-46. LOMO, St. Petersburg, Russia; in quartz cells (l = 1 cm)), between 500 and 800 nm digitized every 5 nm with optical scale (definition) 0,5 nm. pH meter (universal ionometer pH-meter 150 MI, Minsk, Byelorussia) was used for the pH adjustments. The absorbance data from the spectrophotometer were collected in Excel. Analysis was performed in Matlab.

Reagents

Metal ions standard solutions (0,01 mol·L^{-1}) were prepared by the dissolution of metal shots of extra purity in nitric acid.

1-(2-pyridylazo)-2-naphthol (of the "Reanal" company) was additionally purified by recrystallization from isopropanol. A working solution of $4 \cdot 10^{-3}$ mol·L^{-1} concentration was prepared by dissolution of the necessary PAN shot in ethanol and making it up to the mark in a volumetric flask.

The SAS (Surface activity substance) solution – sodium ethoxydodecyl-sulphate with average molar weight of 700 (gel with a mass fraction of the basic substance of 70,1 %, manufacturer: "Cognis") was prepared with a mass fraction ω = 12,5% by dissolution of a shot in a distilled water.

The buffer solution containing 0,05mol/l $Na_2B_4O_7 \cdot 10H_2O$, 0,14 mol·L^{-1} $Na_2HPO_4 \cdot 2H_2O$, 0,2 mol·L^{-1} $Na_3C_6H_5O_7 \cdot 5{,}5H_2O$ and 0,06 mol·L^{-1} NaOH was used.

Procedure generation of two-dimensional spectra

Complex absorption spectra and their yield according to the pH were measured on a spectrophotometer-ionometer apparatus with pH-electrodes in a cell. The titrant (HCl, 0.5 mol·L^{-1}) moved through a flexible capillary from the microburet into a cell. After each step of a titrant addition, pH and absorbance measurements in λ = 520 - 600 nm range were carried out. Such measurements were done for the solution containing cations as well as for the solution in the blank run. After subtraction, the two-dimensional ion-complex absorption spectrum with the PAN according to λ and pH was acquired.

Aliquot part of solutions (no more than 6 ml) (Zn^{2+}, Cd^{2+} and Mn^{2+} cations) are brought into a 25 ml flask. Than 1ml of ascorbic acids (mass fraction is 10 %), 1 ml of the PAN are brought in, than alkali solution (*c*(NaOH) = 1,0 mol·L^{-1}) is added drop by drop until steady red colour occurs, than 10 ml of the buffer and 5 ml of SAS are added. After that the solution is made up to the volume with distilled water. 8 ml of aliquot is placed in a 1 cm-width cell and titrated with hydrochloric acid at 0,05 ml measuring absorbance and pH.

Preliminary correction of the measurement results

Calculations were carried out in Matlab 6.5 software.

The measured values of the array A(i, j) adjusted to reflect changes in the volume of the solution, A^{cor} (i, j), according to the equation (5), and then subjected to a cubic spline approximation - calculated value $A^{(0)}$(n_λ, n_{pH}) for pH_i = 7.0 +0,20 i (i = 0 ... n_{pH})

$$A^{cor}(i,j) = A(i,j) \cdot (V_0 + \Delta V_j) / V_0 \quad (5)$$

where, V_0 = 8,0 ml − volume aliquot of solution complexes; ΔV_j − the added volume of NaOH to the titration of V_0.

Design method

Calibration matrix (**E**(n_1,n_2)) of λ-pH coordinates breaks up in two vectors:

$$\mathbf{E}(n_\lambda, n_{pH}) = \mathbf{V}(n_\lambda, 1) \cdot \mathbf{Q}(n_{pH}, 1), \quad (6)$$

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

Components concentration is obtained by multiplying the two vectors (2):

$$\mathbf{E}(n_\lambda, n_{pH}) = \mathbf{V}(n_\lambda, 1) \cdot \mathbf{Q}(1, n_{pH}) \quad (7)$$

Components concentration is calculated by the following equation (3):

$$\mathbf{c} = \mathbf{V}^+ \cdot \mathbf{A}^{(0)} \cdot (\mathbf{Q}^+)^{\mathbf{T}} \quad (8)$$

where, $\mathbf{A}^{(0)}$ – the matrix of initial absorbance in the analyzed system, ($^+$) – indicates the matrix pseudo inversion $(\mathbf{V}^+ = (\mathbf{V}^{\mathbf{T}} \cdot \mathbf{V})^{-1} \cdot \mathbf{V}^{\mathbf{T}})$

However at such calculation the result will be correct only if $\mathbf{A}^{(0)}$ contains a two-dimensional spectrum of a single determinate component. In a multicomponent analysis determined concentrations are distorted by the presence of other absorptive components. In order to bring test results closer to the actual values it is proposed to use the method of successive approximations (consistent method of incorporating surface).

The first determined component is the one which first shows dependence of yield at the increasing of pH. After the estimation of the concentration by the equation (2), restoration of the response surface is carried out by the equation (4).

$$\mathbf{A1} = \mathbf{V}\ \mathbf{Q}\ \mathrm{c} \quad (9)$$

The **A1** surface in the area where the first component is emerging lies over **A**, and in the area of higher pH, we observe **A1** (i, j) <**A** (i, j). After element replacements by the following condition:

if **A**(i, j) – **A1**(i, j) > 0.001 then $\mathbf{A}^{(1)}$ (i, j) = **A1**(i, j), calculation by the equation (2) is carried out $\mathbf{c}^{(1)} = \mathbf{V}^{+}\mathbf{A}^{(1)} \cdot (\mathbf{Q}^{+})^{\mathrm{T}}$ After *k* successive approximations the result of $c^{(k)}$ does not change.

$^{(1)\,(2)\ldots.\,(k)}$ – number of iteration**.**

The second component concentration is calculated out of the difference matrix $\mathbf{AR}^{(0)} = \mathbf{A}^{(0)} - \mathbf{A}^{(k)}$ by the same algorithm. For the third component of the system the difference matrix $\mathbf{ARR}^{(0)} = \mathbf{AR}^{(0)} - \mathbf{AR}^{(k)}$ is used.

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