Capability of separate determination of colored components in their mixture using digital RGB-colorimetry

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One of the inalienable steps in manufacturing of functional materials is the operational control of traces of toxic heavy metals such as $Fe(III)$ and $Co(II)$ which are present in industrial waste water. The optimal variant for requirements of the analysis in-situ and "green chemistry" is using of environmentally friendly sorbents for preconcentration with simple procurable and portable equipment. Colorimetric characteristics of colored components on the example of thiocyanate complexes of $Fe(III)$ and $Co(II)$ by means of digital RGB-colorimetry have been studied. Algorithm for the colorimetric determination of each of the said components at their joint presence in water using measurements of only three color parameters of the colored mixture was developed. Separation factor of the analytical signal is estimated.

Keywords: color complexes mixture, digital RGB-colorimetry, separate determination, iron; cobalt, polyurethane foam.

Одним из неотъемлемых этапов при производстве функциональных материалов является оперативный контроль микропримесей токсичных тяжелых металлов, таких как $Fe(III)$ и $Co(II)$, которые присутствуют в промышленных сточных водах. Наиболее оптимальным вариантом, удовлетворяющим требованиям анализа на месте отбора пробы и "зеленой" химии, является использование экологически чистых сорбентов для предварительного концентрирования вместе с простым, доступным и портативным оборудованием. Были изучены цветометрические характеристики окрашенных компонентов на примере тиоцианатных комплексов $Fe(III)$ и $Co(II)$ с помощью цифровой RGB-цветометрии. Разработан алгоритм цветометрического определения каждого из указанных компонентов при их одновременном присутствии в воде с использованием измерений только трех цветовых параметров окрашенной смеси. Оценен фактор разделения аналитического сигнала.

Можливості роздільного визначення забарвлених компонентів у їх суміші з використанням цифрової RGB-колометрії. *С.В. Химченко, Л.П. Експеріандова.* Одним з невід'ємних етапів при виробництві функціональних матеріалів є оперативний контроль мікродомішок токсичних важких металів, таких як $Fe(III)$ і $Co(II)$, які присутні в промислових стічних водах. Найоптимальнішим варіантом, що задовольня219 вимогам аналізу на місці відбору проби і "зеленої" хімії, є використання екологічно чистих сорбентів для попереднього концентрування разом з простим, доступним і портативним обладнанням. Були вивчені кольорометричні характеристики забарвлених компонентів на прикладі тіоціанатних комплексів $Fe(III)$ і $Co(II)$ за допомогою цифрової RGB-кольорометрії. Розроблено алгоритм кольорометричного визначення кожного із зазначених компонентів при їх одночасній присутності у воді з використанням вимірювань тільки трьох колірних параметрів забарвленої суміші. Оцінено фактор розділення аналітичного сигналу.   на пінополіуретані. Правильність методики такого роздільного визначення перевірена на зразках природно води за схемою "введено-знайдено".

1. Introduction

One of the inalienable steps in the functional materials manufacturing is the operational control of toxic heavy metals trace in industrial waste water. In particular, in the waste water of such manufacturing the traces of contents of Fe(III) and Co(II) can be presented which are normalized. The known instrumental methods for determination of the heavy metals in water (ICP-AES, AAS) are associated with the use of very expensive equipment that is not readily available for ordinary laboratories, as well as it is not applicable at the non-laboratory analysis. The other methods involve the using of toxic organic extractants which is making their using dangerous to the environment. The optimal variant for the analysis in-situ is using of environmentally friendly sorbents for preconcentration in combination with a simple, as well as procurable and portable equipment.

Chemical digital colorimetry (color measurement) as an instrumental method of analysis has broad capabilities and significant advantages for determining of colored compounds. One of the most important and difficult analytical problem in the colorimetry is the separate determination of the colored substances in their mixture.

Unlike optical spectroscopic methods, in particular, spectrophotometry or diffuse reflectance spectroscopy (DRS), the digital colorimetry does not give data on the spectral characteristics of the colored substances, but characterizes the color by means of set of several numerical parameters. The coloring substance in spectrophotometry corresponds to wavelength of the maximum of light absorption in spectrum. In the colorimetry the coloring substance is determined by the dominant wavelength characterizing wavelength pure spectral color on the graph of CIE 1931 (Commission Internationale de l'Eclairage) [1–3]. Sometimes as parameter characterizing the dominant wavelength is used the hue measured in degrees or nanometers [1].

The authors of [4—7] developed practical ways of the separate colorimetric determination of elements in a mixture of the sorbed colored complexes which are distinguished by the color tone. For this purpose, the definition of the color parameters ΔL (change in of lightness), ΔS (change in saturated) and color coordinates A, B (in the system CIE *LAB*, 1976), the authors of the cited study used data from the DRS received by them with the help of stationary colorimeter "Spektroton". However the complexities of the equipment and the subsequent calculation algorithm of the color characteristics from the diffuse reflection spectrum do not allow the rapid determination of the colored components of mixtures in place of sampling.

The basis of the separate colorimetric determination of colored compounds is the principle of vector addition of analytical signals. And different color parameters, for example, ΔL and ΔS serve as these signals. The vector addition of the analytical signals (for example, the color parameters ΔL or ΔS) is the basic principle for the separate colorimetric determination of the colored compounds. It is known that ΔL and ΔS values have linear dependence on concentration of the colored compound and their proportional increasing or decreasing is observed only in the area of linearity of A and B values [6, 7]. Unlike the CIE *LAB* system characterizing by two selective parameters (A, B) and one non-selective parameter (ΔL), all the *RGB* system parameters (Red, Green, Blue) are selective and depend on the colored compound concentration. Another advantage of the RGB system is the possibility of instrumental (digital) color coordinate measurement with the high accuracy without using diffuse reflectance spectra. It makes the use of the *RGB* system perspective for the mixtures analysis because of completeness of the separate determination of colored components depends on the measurement error of the analytical signal [5]. It is not unimportant that portable digital device application in such a case gives the opportunity to carry out the analysis in the field conditions. Note, the *RGB* system application for the separate determination of colored microimpurities has not been reported in the literature.

The aim of the present work is to test the possibility of colorimetric separate determination of colored components in their mixture on the example of a model mixture of thiocyanate of Fe(III) and Co(II) using three-color digital *RGB*-colorimetry and its comparison with the known DRS method which is used for this purpose.

2. Experimental

2.1. Apparatus and software

The color *RGB* coordinates of samples of polyurethane foam (PUF) were measured and digitized by means of portable reflec-

tometer-colorimeter developed by Analytical Optochemotronics Lab of Kharkiv National University of Radioelectronics [8]. The reflectometer was calibrated using the etalon $BaSO_4$ for diffusion reflectance spectrometry as a standard of white color before the *RGB* measuring. The PUF tablet was placed on the reflectometer glass slide, pressed by the heavy white Teflon plate and it was obtained average values of luminance of channels *R*, *G*, *B*, which are displayed in a dialog window of the software developed by the manufacturer of the mentioned reflectometer. Then by least squares there were calculated coefficients of equations for calibration dependences of luminance of channels *R*, *G*, *B* on concentration of Fe(III) and Co(II).

Measuring the diffusion reflectance spectrum coefficients was carried out on DFS add-on for SF-2000 Bio spectrophotometer with SFScan software. The diffusion reflectance coefficient R_d, measured against to the blank sample containing no analyte served as the analytical signal. Concentrations of Fe(III) and Co(II) were found from the equations of the calibrate dependences of R_d on concentration of the corresponding element.

2.2. Reagents

There were used bidistilled water and the reagents of chemically pure grade to prepare solutions. The standard solutions (Fluka, Switzerland) of 1.00 g·L^{-1} of Co(II) and Fe(III) in 0.001 mol·L^{-1} HNO_3 were used as initial solutions. Working solutions were prepared from the initial solutions by diluting ones with HNO_3 (Merck, Germany) of the same concentration. There were used also solutions of 1.5 mol·L^{-1} KSCN (Fluka, Germany) and 2 mol·L^{-1} H_2SO_4 (Merck, Germany). Solution of KSCN was prepared by dissolving the precisely weighed salt in water.

As a sorbent, we used ether-based PUF of 22-3.0 type. PUF tablets with diameter of 16 mm and 0.025 g were stamped with metal punch from PUF plate with 5 mm thickness. Then tablets were purified by means of their keeping in 1 mol·L^{-1} H_2SO_4 (Merck, Germany) during 1 h and washed with water till obtaining neutral pH and dried in air. The washed tablets were compressed using a glass stick and the rest of the solution removed with filter paper and dried on air.

2.3. Preconcentration procedure

Color comparison scale was prepared according to the known techniques [9, 10]. The analyzed solution with the determined component and required reagents for formation of colored complexes were placed in 50 ml beaker. Then each beaker was added with the PUF tablet prepared as described above and air bubbles were removed by pressing with a glass stick. The obtained solution was stirred for 30 min by means of magnetic stirrer. Then the tablet was removed from the solution, squeezed with a glass stick, the rest of the solution was removed with filter paper and dried in air.

Statistical processing of the measured results was carried out according to the recommendations [11, 12].

3. Results and discussion

3.1. Separate Fe(III) and Co(II) RGB-determination in the model solution

Colorimetry as a physical method of chemical analysis is based on determination of substance concentration by absorption of the light by solutions. In contrast to the physical method of colorimetry, *digital image colorimetry* is based on measurements of color characteristics (color coordinates) of colored components or their images, for example, by means of three-color digital colorimeters.

There were studied the PUF color scales containing sorbed Fe(III) and Co(II) thiocyanate complexes of red and blue color correspondingly [9, 10], as well as the scales containing the mixture of these complexes (Fig. 1). Separate visual determination of these elements in their colored mixture is difficult, because eye can not simultaneously separate and quantify the two color constituents on the scale. Often resort to a preliminary chemical masking of one of the elements, but this procedure complicates the analysis. However, because of the thiocyanate complexes of Fe(III) and Co(II) differ in color, we can pick a pair of common identical parameters *RGB*, which changing with increasing of concentration of the studied elements. For the system of Fe(III)–Co(II) such parameters are *R* and *G*.

To use proposed by the authors [4−7] principle of vector addition of the color characteristics for the colorimetric separate determination of these elements, it was necessary to evaluate the linearity of changes in the parameters *R* and *G* on the whole range of detectable concentrations and to determine the factor of separation of the analytical signal.

Fig. 1. Color scales containing thiocyanate complexes of Fe(III) and Co(II) sorbed on PUF.
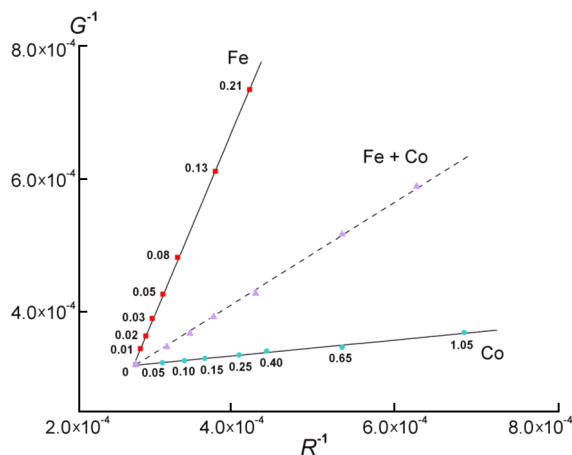

Fig. 2. Diagrams of color parameters $R^{-1} - G^{-1}$ with linearized concentration dependences for Fe(III) and Co(II) thiocyanate complexes and their mixture.

Usually concentration dependences of the color coordinates R, G, B are not linear, and often exponential [13, 14]. The same phenomenon we found also for Fe(III)–Co(II) system. Using the inverse function $f^{-1}(C)$ (where $f = R$, G, B) allowed to linearize the specified dependences in a sufficiently wide concentration range. A similar technique of the linearization was used in [12] for dependence of the relative standard deviation (RSD) on the inverse concentration (C^{-1}) of analyte in solution. Fig. 2 shows the color R^{-1}–G^{-1} diagram with the linearized concentration dependences. One can see that the concentration range of linearity of these dependences for Fe(III) and Co(II) are of 0.01–0.21 and 0.05–1.05 mg·L^{-1}, correspondingly.

As a criterion for completeness of signal separation the authors of [4–7] used factor of separation analytical signal α, which we in the case of analysis of the mixture Fe(III) and Co(II) evaluated using equations (1) proposed in these works:

$$\alpha = \frac{2|k_{Fe} - k_{Co}|}{|k_{Fe}| + |k_{Co}|}, \qquad (1)$$

where $0 \leq \alpha \leq 2$, k_{Fe} and k_{Co} — slope ratio of change of the color coordinates in calibration equations of vs. the Fe(III) and Co(II) concentrations respectively. The factor of separation (in degrees) was calculated using equations (2):

$$\beta = |\text{arctg} k_{Fe} - \text{arctg} k_{Co}|. \qquad (2)$$

Values of slope ratio in the equations of color coordinate change $\Delta R^{-1}(C)$–$\Delta G^{-1}(C)$ were found as $k_{Fe} = 2.94$ and $k_{Co} = 0.12$ for Fe(III) and Co(II), respectively. The separation factor of the signal for Fe(III) and Co(II) was found of $\alpha = 1.7$ or in degrees of $\beta = 53.6°$ (equations 1, 2). Obtained are the values of $\alpha \geq 1$ and $\beta > 25$ corresponding to the values of the factors of colorimetric separation

α and β for satisfactory separation of the components which are given in the publications [4, 6, 7] with colorimeter "Spektroton". In the same article it was notised that the criteria for satisfactory separation of the signal α and β depend on error of the color coordinates measurement. So it is understandable why the measurement accuracy of the analytical signal, as mentioned above, influences on the completeness of the digital colorimetric separation. In this study the measurement results of any of the channels R, G, B characterized RSD 0.01–0.04 for the entire range of concentrations.

Note, however, that more rigorous and at the same time universal assessment of the effectiveness of such a separation would be more correct to do on the basis of statistical criteria, for example, such as recommended for evaluating the limits of determination and detection [12]. Apparently, the role of this criterion may perform the summary value of relative standard deviation of the measured signal that not exceeding 0.33, above which the separation ceases to be quantitative.

Next, using the law of vector addition of analytical signals [4, 6, 7], we obtained a system of the 4th order nonlinear algebraic equations (3) and (4).

$$\Delta G^{-2} = (2.00 \cdot 10^{-3} C_{Fe})^2 + \qquad (3)$$
$$+ (5.09 \cdot 10^{-6} + 4.53 \cdot 10^{-5} C_{Co})^2,$$

$$\Delta R^{-2} = (6.83 \cdot 10^{-4} C_{Fe})^2 + \qquad (4)$$
$$+ (1.83 \cdot 10^{-5} + 3.65 \cdot 10^{-4} C_{Co})^2,$$

Table 1. Analysis results obtained by means of digital *RGB*-colorimetry and DRS for Fe(III) and Co(II) in the model solutions ($P = 0.95$; $n = 5$)

No.	C_{added}, mg·L^{-1} Fe(III)	C_{added}, mg·L^{-1} Co(II)	C_{found} (RGB), mg·L^{-1} Fe(III)	RSD	C_{found} (RGB), mg·L^{-1} Co(II)	RSD	C_{found} (DRS), mg·L^{-1} Fe(III)	RSD	C_{found} (DRS), mg·L^{-1} Co(II)	RSD
1	0.01	0.05	0.010 ± 0.001	0.21	0.054 ± 0.007	0.18	0.013 ± 0.011	1.0	0.20 ± 0.20	1.2
2	0.02	0.10	0.020 ± 0.003	0.24	0.11 ± 0.01	0.17	0.021 ± 0.011	0.6	0.27 ± 0.19	0.8
3	0.03	0.15	0.033 ± 0.005	0.23	0.17 ± 0.02	0.15	0.034 ± 0.019	0.7	0.42 ± 0.31	0.8
4	0.05	0.25	0.050 ± 0.008	0.22	0.28 ± 0.03	0.13	0.047 ± 0.029	0.7	0.60 ± 0.34	0.6
5	0.13	0.65	0.13 ± 0.01	0.09	0.67 ± 0.02	0.04	0.13 ± 0.03	0.3	1.48 ± 0.39	0.3
6	0.21	1.05	0.21 ± 0.01	0.06	1.06 ± 0.04	0.05	0.16 ± 0.02	0.13	1.79 ± 0.31	0.2

where C_{Fe} and C_{Co} are Fe(III) and Co(II) concentrations, respectively.

For solving this system of nonlinear algebraic equations with two unknown parameters we used the Newton calculation method and SciLab 5.2.1 software. Table 1 shows the content of Fe(III) and Co(II) in the model solutions which have been found from the equation system. As can be seen from Table all element concentrations found by *RGB*-colorimetry taking in account their confidence intervals coincide with the introduced. This confirms the correctness results of colorimetric determination of these elements.

It is known that mixing of two or more colors is realized in two main ways — additive and subtractive [2, 3]. The additive color mixing occurs if reflecting the light surface is evenly colored by components with the various color tone (hue). The subtractive color mixing in the reflected light occurs if light is passing to observer through a few successive color layers of the surface. At an ideal thin reflective layer the contribution of subtractive mixing is infinitely small, but due to heterogeneity of real surfaces, transparence and irregularity of the coloration, this contribution is always present. Therefore practically insignificant deviation toward the overstatement content of Co(II) at high concentrations (Table 1) may be explained by appearance of small deviations from the additivity law of the analytical signal in this area. It should be noted that the experimental check of the signal additivity at the determination of components in a mixture not carried by the authors but they just assumed the signals additivety in the studied linear part of the concentration range. Methods for detecting deviations from additivity using chemomet-

ric algorithms considered in detail by the authors [15, 16].

Permissible ratios of the colored components mixture that can be separately determined using the proposed algorithm were found. For a pair Fe/Co they are in the range of 1:5–4:1 and the random error is less if Co(II) is present in excess. According to Table 1 the error in determining the elements depend on the content generally of each of them and they are, of course, so much the greater than the less contents.

3.2. Separate determination of Fe(III) and Co(II) in the model solutions by means of DRS

The same color scales on the PUF that were studied colorimetrically, was used to study by the method of DRS. Usually in the DRS as the analytical signal it is used the function of Gurevich-Kubelka-Munk $F = (1 - R_d)^2/2R_d$, that depends on the diffuse reflectance, R_d and changing, as a rule, linearly with increasing concentration of the analyte. However in our case of dependence $F - C_{Fe,Co}$ appeared to be nonlinear in contrast to the linear dependences of $R_d - C_{Fe,Co}$, therefore the latter were taken for further calculations. Nonlinearity of the function F, apparently connected with the heterogeneity of the surface, with the transparency (with finite thickness) of the measured samples of PUF and with contribution of the specular component into the total value of the diffuse reflectance coefficient.

Fig. 3 shows the diffuse reflectance spectra of PUF tablets containing the mixture of thiocyanate complexes of the elements under study. The wavelengths for Fe(III) $\lambda = 470$ nm and for Co(II) $\lambda = 618$ nm corresponding to the minima of R_d in the spectrum were chosen as analytical. Thus, for the system of

Table 2. Estimation of accuracy of the separate Fe(III) and Co(II) determination in natural water ($P = 0.95$; $n = 5$)

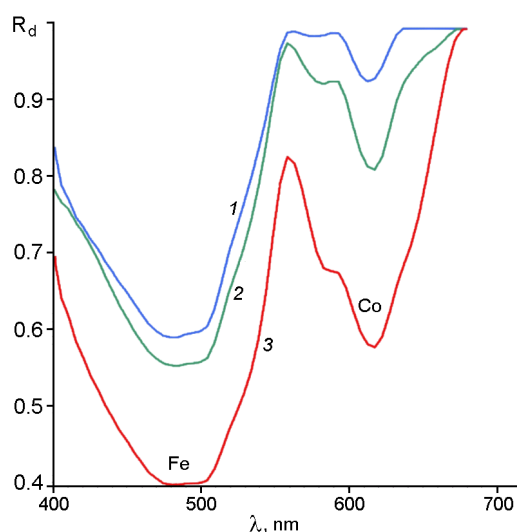| Determined component	C_{added}, mg·L^{-1}	C_{found} (RGB), mg·L^{-1}	RSD	C_{found} (DRS), mg·L^{-1}	RSD	C_{found} (XRF), mg·L^{-1}	RSD	Note
Fe(III)	0.08	0.08 ± 0.01	0.08	0.08 ± 0.02	0.22	0.085 ± 0.005	0.06	Well of Institute for Single Crystals
Co(II)	0.40	0.44 ± 0.05	0.06	0.89 ± 0.10	0.10	0.40 ± 0.05	0.12	
Fe(III)	0.10	0.11 ± 0.01	0.13	0.10 ± 0.02	0.18	0.103 ± 0.005	0.05	Underground water ("Rogan" 700 m)
Co(II)	0.50	0.52 ± 0.03	0.06	1.26 ± 0.07	0.06	0.50 ± 0.06	0.13	

Fig. 3. Diffuse reflectance spectra for PUF tablets containing mixture of thiocyanate complexes of Fe(III) and Co(II).

Fe(III)–Co(II) the difference in position of the maxima in the spectra was $\Delta\lambda = 148$ nm, and it would have to provide satisfactory results of the separate determination elements by means of DRS, that is confirmed by the separation factor obtained by means of the digital colorimetry.

However some values of the relative standard deviation exceeded 30−50% as it is seen from Table 1 showing the found concentration of Fe(III) and Co(II) in the model solutions by means of DRS from the equations of calibration dependences. This means that corresponding concentrations are lay below detection limit [12]. Furthermore, as seen from the same Table, the results for Co(II) obtained by DRS are substantially inflated. Therefore, we can conclude that the method of diffuse reflectance spectroscopy is of little use for separate de-

termination of Fe(III) and Co(II) in their mixture on the PUF.

3.3. Separate determination of Fe(III) and Co(II) in the natural water

Validation of the separate determination of Fe(III) and Co(II) was carried out on "added-found" scheme by introducing additives of the investigated elements in the natural water samples. The analysis results for Fe(III) and Co(II) obtained by means of digital *RGB*-colorimetry and DRS, as well as by independent X-Ray fluorescence method (XRF) with sorption pre-concentration are shown in Table 2.

Table 2 shows that all concentrations of Fe(III) and Co(II) which have been found using digital *RGB*-colorimetry and XRF methods practically coincide with the introduced that confirms the correctness of the results of their determination. According to Table 1 and Table 2 the DRS method in the case of determining Co(II) gives overestimated results that, in addition, have significantly larger errors than those obtained by means of digital *RGB*-colorimetry.

Thus, it is developed and tested the method of separate determination of colored components in their mixture by means of trichromatic digital *RGB*-colorimetry characterized by the greater accuracy, accessibility of equipment and simplicity unlike DRS method.

4. Conclusions

It is shown that method of digital *RGB*-colorimetry for the separate determination of Fe(III) and Co(II) in their mixture on the PUF is notable more accurate and correct results than the DRS method. The main advantage of the method proposed in first time is simplicity, small measurement error *RGB*-coordinate of mixture of the colored complexes and rapid finding concentrations of the components of said mixture. Such

analysis is carried out using of preliminary obtained calibration curves as it is usual done in the analytical practice. The big advantage of such colorimetric analysis is the exclusion of the application of the spectrometer with the integrating sphere and further spectrum treatment which are required in the case of DRS that greatly simplify the analysis.

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