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Colorimetric scales for chemical analysis on the basis of transparent polymeric sensors

Sergey V. Muravyov, Natalya A. Gavrilenko, Anna S. Spiridonova
Stanislav V. Silushkin and Peter G. Ovchinnikov

Department of Computer-aided Measurement Systems and Metrology
Tomsk Polytechnic University
Tomsk, 634050, Russia

muravyov@camsam.tpu.ru

Abstract – Results are presented of implementing a new kind of optical analytical method, in which, as a sensor, membranes are used that are created of reagents immobilized on optically transparent solid polymer matrices. Interacting with a substance under investigation the immobilized reagents change the matrix color. This color change indicates a content of a component determined and persists for a long time. The color difference obtained can be transformed to numerical value that is treated as analytical information. The registration of not reflection and transmission of the light radiation through transparent sensor is promising to reach larger sensitivity up to order of magnitude 10^2 at low optical absorption.

1. Introduction

Rapid analytical testing [1, 2] is required in different production processes (for example, in inspection of water chemistry of power installations, water cleaning and water conditioning); in environmental monitoring; in biometric and biomedical analysis (for instance, blood test for lithium ions, specific proteins, vitamins, etc.). In the class of optical analytical methods the spectrophotometry is traditionally used. In this case, optical density or transmission of solutions are evaluated with subsequent their recalculation in terms of parameters of substances under investigation sought for. Frequently, the optical spectrum obtained is so complicated that cannot be easily interpreted. Also, traditional spectrophotometers needs a sample preparation and have unsatisfactory mass and dimensional characteristics (5-8 kg) that restricts their applications to large scale quick tests.

2. Polymeric optodes

In order to produce optodes that virtually are a transparent polymeric material containing functional groups being able to sorb and extract analytical reagents, and also determined substances, Gavrilenko et al. [3-5] developed a special original technique and laboratory installation. By means of the installation a radical block polymerization of a methacrylic monomers is fulfilled in form of plates 0.5-0.6 mm thick. Then the plates are parted into necessary size chips. Each of the chips is the *polymethacrylate matrix* (PMM).

Then the *immobilization* of analytical *reagents* in a static mode is implemented where the PMM is exposed in water, water-organic or organic reagent solutions for 5-15 min (figure 1). After the immobilization, the matrix remains transparent and uncolored.

As a result of the *contact* of the matrix with the solution containing determined component, in the PMM, under certain pH, a *colored coordinatively saturated complex* is formed, a color of which is in one-

to-one correspondence with the content C of the determined component in a sample. A particular color depends mainly on the reagent and determined component, and its *luminosity* – on the component amount.

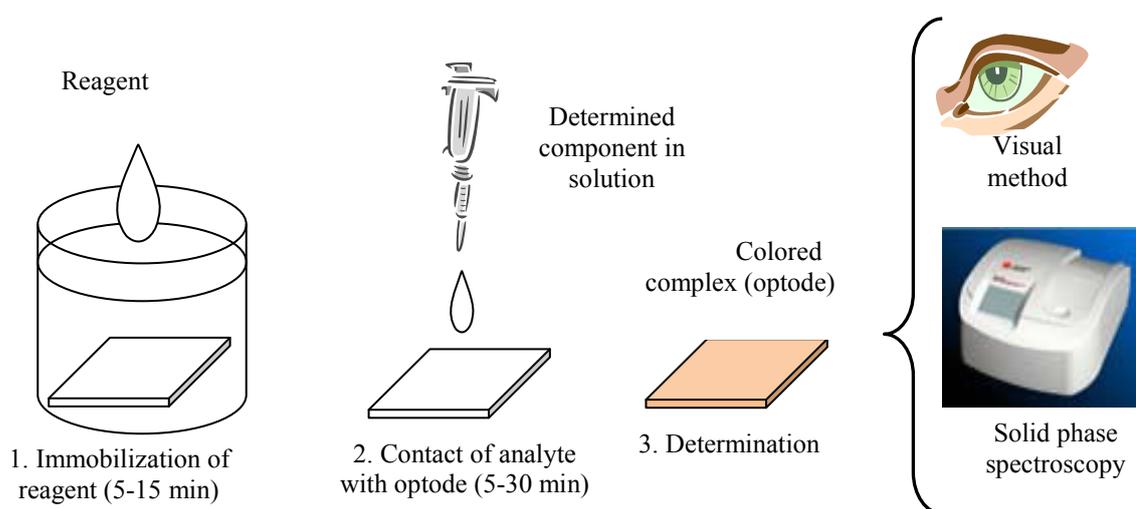


Figure 1. Stages of obtaining the polymeric optodes.

The *absorption spectrum* of the matrix has a maximum corresponding to the wavelength λ_{\max} defining its color. For example, in table 1 some of metals are shown as determined components and their appropriate analytical reagents, optode colors and absorption spectrum maximums.

Table 1. Reagents immobilized into optodes to be intended to determine some of metal ions.

Metal	Reagent	Short name	Optode color	λ_{\max} , nm
Ni (II)	1-(2-pyridylazo)-2-naphtol	PAN	crimson	525, 565
Cu (II)	Pb(II)-diethyldithiocarbamate	Pb(Dtc) ₂	yellow brown	430
Ag (I)	dithizone	DThZ	red violet	520
Fe (II,III)	2,2'-dipyridyl	2,2'-dip	red	520
	1,10-phenantroline	1,10-phen	orange	510

Previous investigations [3-5] have shown that the absorption spectra of the modifying reagents and analytical reaction products generated in a solid phase under contact with determined component, in a solution and in the PMM coincides. The reagents immobilized and analytical reaction products have no effect on the PMM transparency what enables to carry out direct measurement of its optical characteristics at high accuracy.

The optodes developed were tested in practical techniques for detection of Fe (II, III) and chlorides in mineral water, Cu (II) and Ag (I) in drinking tap water, ascorbic acid in orange juice, fluorides in toothpaste and shown highly satisfactory outcomes [4-5].

The transparent polymeric optodes changing dye can be applied both in solid phase spectrophotometry and in visual rapid determination of substances. The latter can be automated using different means of color images capturing by a computer and their subsequent digital processing. This

gives a base to develop a new analytical method, Digital Color Analysis (DCA) [2, 6-7]. This approach is discussed in the next sections of the paper.

3. Colorimetric scale

An optical signal of the polymeric optode to be inputted into the computer can be digitized by means of a color sensor or even usual office scanner (see figure 2).

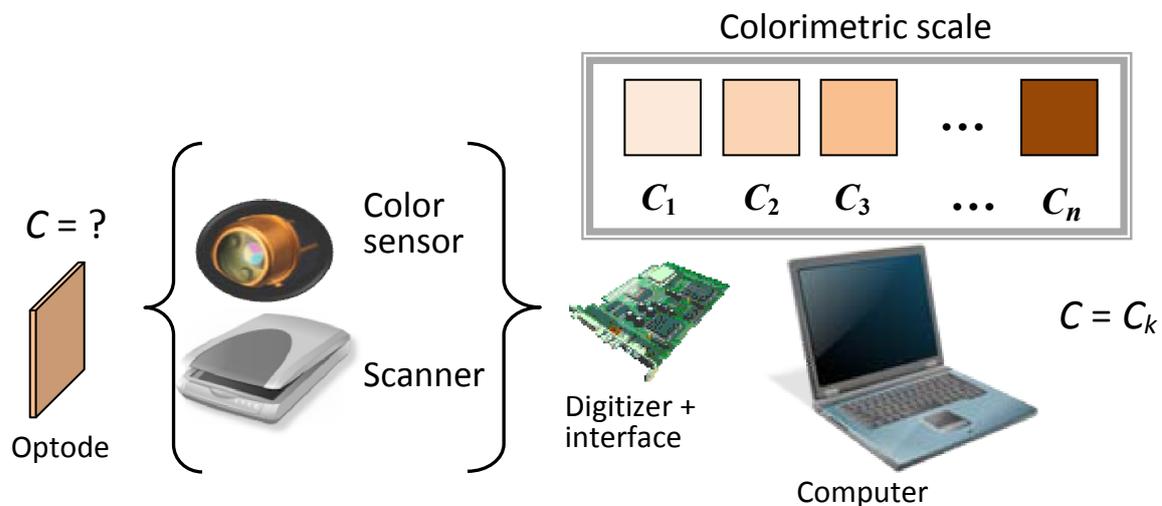


Figure 2. Generalized structure of Digital Color Analysis.

In both computerized and non-computerized visual determination, in order to assign a content value to the given determined component (optode) it is necessary to have a *colorimetric scale* representing a set of *reference color samples*, luminosity of which corresponds to known values of concentration C_k , $k = 1, \dots, n$, where n is a number of the reference samples. The scales can be obtained by means of scanning the reference samples used at plotting the *calibration curves* under solid phase spectrophotometric determination. After capturing the sample colors by the computer and setting up the appropriate concentration values, a storage of the reference samples becomes to be not necessary.

A formal statement of the DCA problem can be as follows. Let $A = \{a_1, a_2, \dots, a_n\}$ be a set of the coordinates describing the reference sample colors; $C = \{c_1, c_2, \dots, c_n\}$ be a set of determined component concentration values assigned to the reference color samples, and n be the number of reference samples. Then the *colorimetric scale* will be called the mapping

$$S = \begin{pmatrix} a_1 & a_2 & \dots & a_n \\ c_1 & c_2 & \dots & c_n \end{pmatrix} \quad a \in A, c \in C. \quad (1)$$

Let x_i be the determined component ($i = 1, \dots, m$, where m is a total number of determined components for the given analytic environment) and C_{x_i} be its sought content.

Then the DCA problem is to find a nearest by the reference sample color to the given optode, that is

$$C_{x_i} = \arg \min_{a \in A} D(a, a_{x_i}), \quad (2)$$

where $D(a, a_{x_i})$ is a distance function (color difference) between color a_{x_i} of the optode and color a of

the reference sample.

In practice, the *color difference* dE can be computed in the RGB color space by the formula (see, for example, [8]):

$$D = dE = \sqrt{D_R^2 + D_G^2 + D_B^2}, \quad (3)$$

where $D_R = R_0 - R$, $D_G = G_0 - G$, $D_B = B_0 - B$; R_0, G_0, B_0 are color coordinates of samples after contact with a plain solution; R, G, B are color coordinates of samples after contact with the solution containing the substance under determination.

4. Experiment: Determination of cobalt

The proposed DCA on the basis of polymeric optodes was implemented by the paper authors using two techniques by means of:

- the evaluation board modEVA with MTCSiCS color sensor produced by MAZeT GmbH (Jena, Germany) and computing the color difference dE by the formula (3) and
- the office scanner *HP Scanjet* in color mode *RGB* 24 bits with resolution 300 dpi and graphic editor *Adobe Photoshop*. The latter allows to select a work channel that is one of the RGB coordinates (*red R* in the case of cobalt) for which the calibration curve has a most slope.

The two approaches results were compared with the solid phase spectrophotometry outcomes where optode absorbance was measured at absorption spectrum maximum $\lambda = 620$ nm (A_{620}) using the spectrophotometer *Spekol 21* for different determined components. It turned out that in all cases metrological performance of the DCA method is not worse than that of the solid phase spectrophotometry. This can be seen from table 2 and table 3 where the comparative data are reduced concerning the DCA and the solid phase spectrophotometry using for cobalt determination in the vitamin B12 ampoule (cyanocobalamin) and in drinking tap water.

Table 2 represents the parameters of calibration graphs and the limits of detection calculated according to the $3s$ -test. The calibration graphs for Co in the form of functional connection $A_{620} = f(C)$, $R = f(C)$, $dE = f(C)$ are shown in figure 3.

Table 2. Calibration curves for cobalt determination.

Measurand	Calibration curve	Correlation coefficient r	Range of determined concentrations, mgL^{-1}	Limit of detection, mgL^{-1}
DCA: color difference dE	$dE = 2.115 + 338.1 \cdot C_{\text{Co}}$	0.986	0.05 – 0.25	0.02
Work channel R	$R = 256 - 213 \cdot C_{\text{Co}}$	0.950	0.05 – 0.25	0.07
Spectrophotometry: optical density A_{620}	$A_{620} = 0.03 + 0.40 \cdot C_{\text{Co}}$	0.999	0.05 – 0.50	0.03

The experiment details are discussed below.

4.1. Reagents

The starting solution of cobalt with a metal concentration of 1 mg/mL was prepared by dissolving a precise weight of cobalt sulfate in water. The working solutions of cobalt with lower concentrations were prepared by the consecutive dilution of the stock solution in the day of experiments. The 1-(2-pyridylazo)-2-naphthol (PAN) solution (0.001 mol/L) was prepared by dissolving a precise portion in ethanol. The

working solution of PAN for immobilization was prepared by the dilution of the 0.001 mol/L solution fourfold with water. All reagents were of chemically pure or analytical grades and used without additional purification.

Table 3. Determination of cobalt in cyanocobalamine (medicinal preparation) and drinking tap water (samples volume $n = 3$, confidence level $P = 0,95$).

Object under investigation	Added, mgL^{-1}	Measurand	Found, mgL^{-1}	Standard deviation σ , %
Cyanocobalamine	-	dE	26 ± 3	4.8
		R	27 ± 4	5.6
		A_{620}	22 ± 5	9.5
Drinking tap water	0.25	dE	0.26 ± 0.02	3.4
		R	0.21 ± 0.02	4.0
		A_{620}	0.25 ± 0.05	7.6

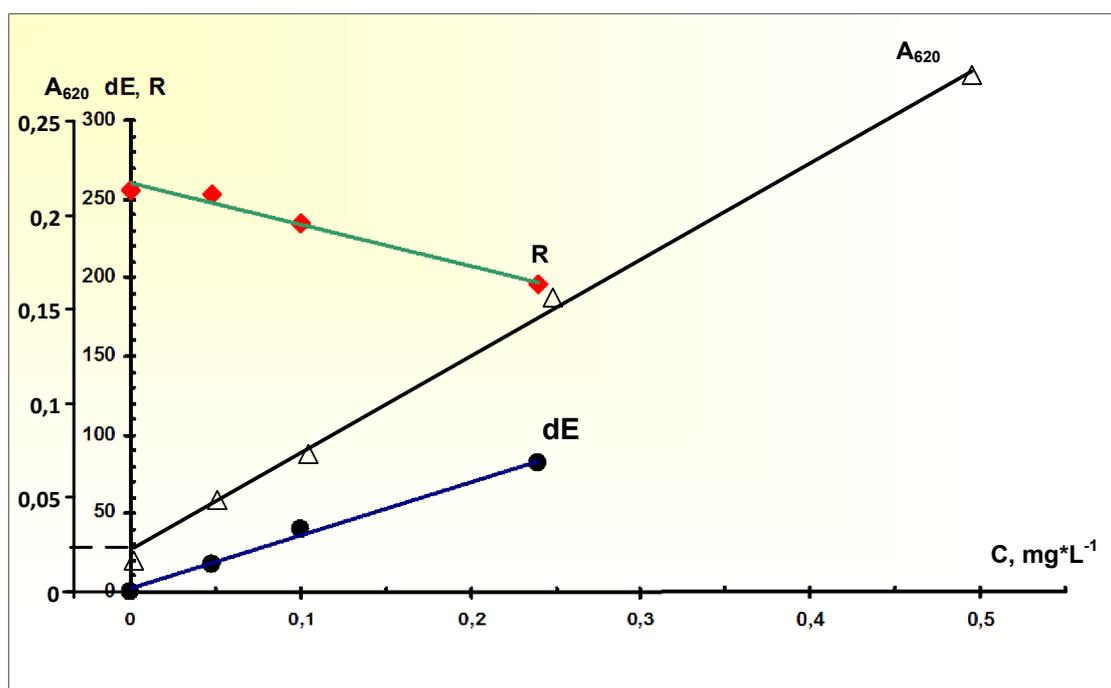


Figure 3. Calibration curves for the three types of analytical signal: color difference dE , work channel R and optical density A_{620} .

4.2. Preparation of polymethacrylate matrix with immobilized PAN

The polymethacrylate matrix as a transparent plate (0.60 ± 0.04) mm thick was prepared by radical block polymerization according to [3]. Then, the plate prepared was cut to make smaller articles of measuring 6.0×8.0 mm. PAN was immobilized into a polymethacrylate matrix by adsorption from the water-ethanol solution in the batch mode. Therein, 25 mL of the reagent solution was stirred with polymethacrylate cuts for 1 min; the matrix turned orange.

4.3. Determination of cobalt in the vitamin B12 ampoule (cyanocobalamine) and in the tap water

A sample was prepared as follows: 12 mL of vitamin B12 ampoules were placed into a porcelain cap, containing 2 mL concentrated sulphuric acid, and then the mixture was heated gently and evaporated to nearly dry. The residue was diluted to 50 mL with water and then an appropriate aliquot was taken for analysis by the recommended procedure. Tap water samples were used directly after running for more than 30 min.

4.4. Recommended procedure for determination of cobalt

A solution to be analyzed was placed in a 50 mL volumetric flask, pH 4 was adjusted by adding NaOH or HCl (checked by a pH meter), the resulting mixture was diluted to the mark with water. A cut of a polymethacrylate matrix with immobilized PAN was put into the solutions followed by stirring for 5 min; then the cut was removed, dried with a piece of filter paper and analytical signal based on A_{620} , R , dE was measured. The concentration of cobalt was calculated with the use of the calibration plots constructed under similar conditions.

5. Conclusion

The polymeric optodes and DCA described in the paper can provide the following advantages as compared with other analytical methods:

- use of colorimetric characteristics allows to increase detection sensitivity and decrease the limit of detection in comparison with solid phase spectrophotometry;
- no necessity to have skilled laboratory support and a sample preparation;
- colorimetric signal appears after short-term contact the polymeric optode and object under investigation and can be stored for a long time;
- the colorimetric data enable effective computer implementation of the analytic methods.

References

- [1] Kaneko E 2004 Development of visual analytical methods for trace determination *Analytical Sciences* **20** 247–54
- [2] Hirayama E, Sugiyama T, Hisamoto H and Suzuki K 2000 Visual and colorimetric lithium ion sensing based on digital color analysis *Analytical Chemistry* **72** 465–74
- [3] Patent 2272284 2004 (Russian Federation) *The indicator sensitive material for determination of microquantities of substances* (Gavrilenko N A and Mokrousov G M)
- [4] Gavrilenko N A and Saranchina N V 2009 Analytical properties of 1-(2-pyridylazo)-2-naphthol immobilized on a polymethacrylate matrix *Journal of Analytical Chemistry* **64** 3 243–7
- [5] Gavrilenko N A, Saranchina N V and Mokrousov G M 2007 A Sensitive Optical Element for Mercury (II) *Journal of Analytical Chemistry* **62** 9 832–6
- [6] Muravyov S V, Gavrilenko N A, Spiridonova A S and Silushkin S V 2009 Digital color analysis for chemical measurements based on transparent polymeric optodes *Proc 9th International Symposium on Measurement Technology and Intelligent Instruments (Saint-Petersburg, Russia)* vol 3 (Saint-Petersburg: D.S. Rozdestvensky Optical Society) pp 138–42
- [7] Kompany-Zareh M, Mansourian M and Ravaee F 2002 Simple method for colorimetric spot-test quantitative analysis of Fe(III) using a computer controlled hand-scanner *Analytica Chimica Acta* **471** 1 97–104
- [8] Sharma G ed 2003 *Digital Color Imaging Handbook* (Boca Raton: CRC Press)