

Digital color analysis for chemical measurements based on transparent polymeric optodes

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Abstract

The paper is devoted to tentative results of implementing a new kind of optical analytical method – digital color analysis (DCA), in which, as an optode, 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. DC-analyzer works in similar way as the human eye which rather precisely discriminates colors in spite of a possible spectral complexity of the optical signal. The registration of not reflection and transmission of the light radiation through transparent optodes is promising to reach by 1-2 orders of larger sensitivity at low optical absorption.

Keywords: Polymeric optode, digital color analysis, colorimetric scale

1. Introduction

Rapid analytical testing [1, 2] is required in different production processes (for example, in inspection of water chemistry conditions 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. [3-6] 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 (see Fig. 1) 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. After the immobilization, the matrix remains transparent and uncolored.

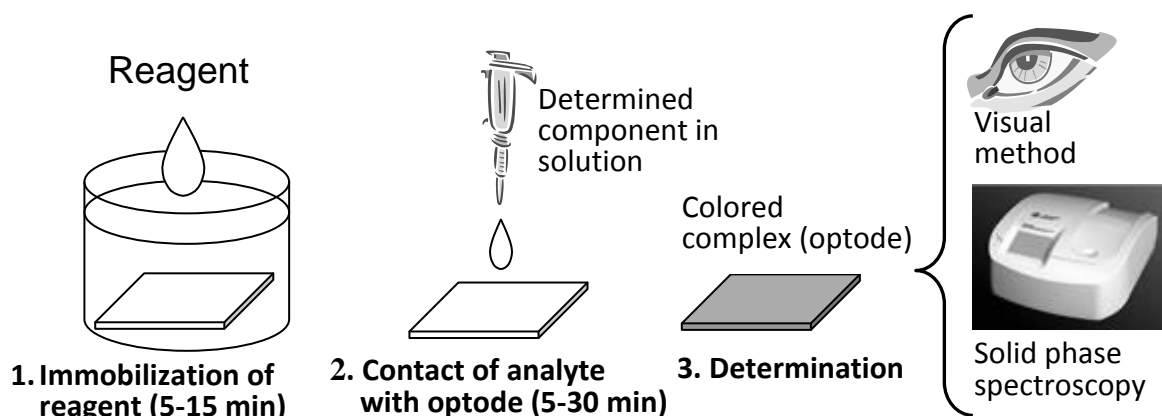


Fig. 1. Obtaining sequence an application of the polymeric optodes.

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 mapping 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. 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(Ddte) 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 [3-6] 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 [4-6].

The transparent polymeric optodes changing dye can be applied both in solid phase spectrophotometry and in visual rapid determination of substances (Fig. 1). 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). This approach is discussed in the next sections of the paper.

3. Digital color analysis

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

3.1. Colorimetric scale

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.

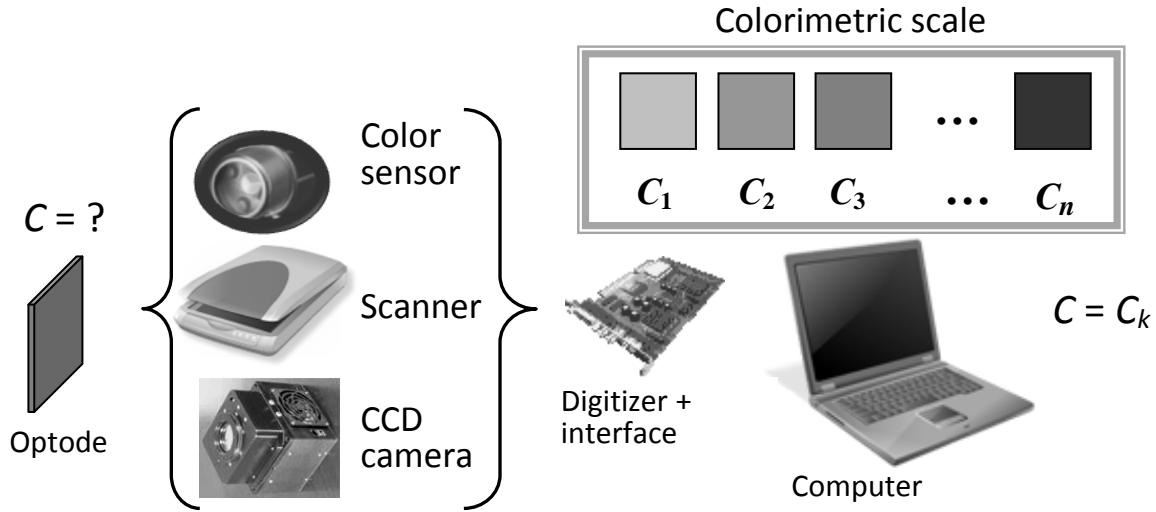


Fig. 2. Generalized structure of Digital Color Analysis.

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 work channel coordinates describing the reference sample colors (the *work channel* will be called the coordinate of a standard color system for which the calibration curve has a most slope), $C = \{c_1, c_2, \dots, c_n\}$ be a set of determined component concentration values assigned to the reference color samples, and n be the number of reference samples. 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. Clear that (see Section 2)

$$C_{x_i} = f(S_i, R_i, Y_i), \quad (2)$$

where S_i is the colorimetric scale; S_i is the reagent; Y_i is the optode color.

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

$$C_{x_i} = \arg \min_{a \in A} D(a, a_{x_i}), \quad (3)$$

where $D(a, a_{x_i})$ is a distance function (color difference) between color of the optode and that of the reference sample. Clear that a way to calculate $D(a, a_{x_i})$ depends on the color representing system chosen.

3.2. Color representing system choice

In order to estimate opportunities of a use in the DCA, four standard color systems were investigated: *RGB*, *HSL*, *CIE Lab* и *CIE XYZ*. For the determined metals, Cu (II), Ag (I) and Fe (II,III), were revealed the work channels *A*, plotted calibration curves and computed respective correlation coefficients ρ . The data obtained are reduced to Table 2.

Table 2. Color representing systems for visual determination of copper, iron and silver.

| Color system | Cu (II) | | | Fe (II) | | | Ag (I) | | |
|----------------|----------|--------------------|--------|----------|-------------------|--------|----------|-------------------|--------|
| | <i>A</i> | Calibration curve | ρ | <i>A</i> | Calibration curve | ρ | <i>A</i> | Calibration curve | ρ |
| <i>RGB</i> | <i>B</i> | $y = 239 - 2330 C$ | 0.9977 | <i>G</i> | $y = 194 - 30 C$ | 0.9964 | <i>G</i> | $y = 229 - 169 C$ | 0.988 |
| <i>HSL</i> | <i>S</i> | $y = 23 + 779 C$ | 0.9878 | <i>S</i> | $y = 206 - 27 C$ | 0.8292 | <i>S</i> | $y = 27 + 88 C$ | 0.9553 |
| <i>CIE Lab</i> | <i>b</i> | $y = 11 + 243 C$ | 0.9766 | <i>a</i> | $y = 234 - 15 C$ | 0.8177 | <i>L</i> | $y = 238 - 44 C$ | 0.9591 |
| <i>CIE XYZ</i> | <i>Z</i> | $y = 1 - 9 C$ | 0.9976 | <i>Y</i> | $y = 0.8 - 0.2 C$ | 0.8367 | <i>Z</i> | $y = 0.9 - 0.5 C$ | 0.989 |

From comparison of the correlation coefficients values of Table 2 it follows that, in this particular case, the use of the *RGB*-model is most preferable for the DCA. However, one should take into account that a uniform-chromaticity color system is needed to evaluate color differences [7]. Unfortunately, the four systems discussed dissatisfy this requirement. That is why the issue of most suitable color system for the DCA must be further studied.

3.3. The DCA software

A tentative software project for the DCA has been implemented in the graphic package LabVIEW (Fig. 3). It enables to measure a color in the *RGB* space, and also to represent the color in systems *HSL*, *CIE Lab* and *CIE XYZ*; to create, store and indicate a colorimetric scale for each of determined substances; to implement various algorithms for the problem (3) solving, and also color difference calculations.

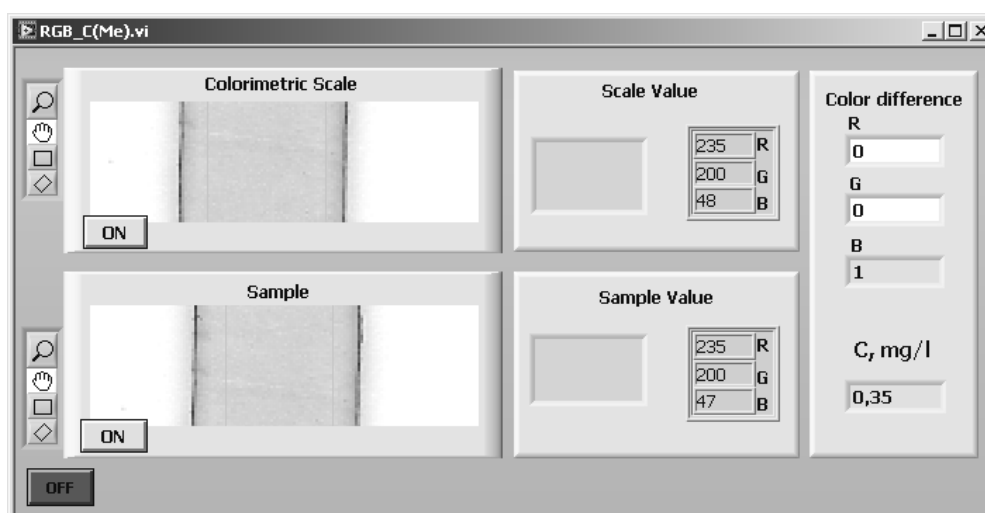


Fig. 3. User interface of the LabVIEW program for DCA.

The developed program provides an illustrative demonstration of interrelations between the luminosity in the system *RGB* and the optode color. Indeed, with increasing a concentration of copper, accompanied by a color intensity growth, the color images brightness of *R*, *G* and *B* channels decreases. The latter is caused by decreasing white fraction in the optode color.

3.4. Comparison of DCA and spectrophotometry

Most simple and inexpensive way of DCA implementation is a use of

- an office scanner as a tool for the optode color image input to the computer and
- the image editor Adobe Photoshop as a software.

This approach was used by authors of the paper to compare the DCA and the solid phase spectrophotometry for different determined components. It turned out that in all cases their metrological performance of both of the methods is of the same level. This can be seen, for example, from Table 3 where the comparative data are reduced concerning the CDA and the solid phase spectrophotometry using for copper determination.

Table 3. Metrological performance of Cu (II) determination.

| Attributes | Spectrophotometry | DCA |
|------------------------------------|---------------------------|--------------------|
| Calibration curve | $A_{430} = 0.07 + 1.70 C$ | $B = 239 - 2330 C$ |
| ρ | 0.9932 | 0.9977 |
| Range of determined concentrations | 0.05-1.0 | 0.05-1.0 |
| Limit of detection | 0.02 | 0.01 |

In Table 4 an example is given on validity check of the determination of copper content in two samples of tap water.

Table 4. Validity check of copper determination in tap water.

| Object | Added, mg dm ⁻³ | Spectrophotometry | | DCA | |
|----------|----------------------------|----------------------------|--------------------|----------------------------|--------------------|
| | | Found, mg dm ⁻³ | Standard deviation | Found, mg dm ⁻³ | Standard deviation |
| Sample 1 | 0 | 0.03 ± 0.02 | 0.41 | < 0.02 | 0.5 |
| | 0.3 | 0.34 ± 0.05 | 0.13 | 0.29 ± 0.07 | 0.10 |
| Sample 2 | 0 | 1.02 ± 0.13 | 0.10 | 1.09 ± 0.12 | 0.09 |
| | 0.3 | 1.26 ± 0.17 | 0.11 | 1.32 ± 0.09 | 0.12 |

4. Conclusion

The polymeric optodes and DCA described in the paper can provide the following advantages as compared with other analytical methods: 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. E. Kaneko. *Development of visual analytical methods for trace determination*. Analytical Sciences. 2004, vol. 20, pp. 247-254.
2. E. Hirayama, T. Sugiyama, H. Hisamoto, K. Suzuki. *Visual and colorimetric lithium ion sensing based on digital color analysis*. Analytical Chemistry. 2000, 72, pp. 465-474.
3. Patent № 2272284, 2004 (Russian Federation). *The indicator sensitive material for determination of microquantities of substances* (N.A. Gavrilenko, G.M. Mokrousov).
4. N.A. Gavrilenko, G.M. Mokrousov, O.V. Dzhiganskaya. *Journal of Analytical Chemistry*. 2004, vol. 59, No. 9, pp. 871-874.
5. N.A. Gavrilenko, N.V. Saranchina. *Analytical properties of 1-(2-pyridylazo)-2-naphthol immobilized on a polymethacrylate matrix*. *Journal of Analytical Chemistry*. 2009, vol. 64, No. 3, pp. 243-247.
6. N.A. Gavrilenko, N.V. Saranchina, G.M. Mokrousov. *A Sensitive Optical Element for Mercury (II)*. *Journal of Analytical Chemistry*. 2007, 62(9), pp. 832-836.
7. G. Sharma (Ed.) *Digital Color Imaging Handbook*. CRC Press, Boca Raton, USA. 2003.