

COLORIMETRIC POLYMER SENSOR FOR DETERMINATION OF CHROMIUM (VI): COMPARISON OF ESTIMATION METHODS OF THE VISIBLE COLOR CHANGES

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Abstract – The paper describes an application of a kind of optical analytical method, digital color analysis (DCA), using colorimetric polymethacrylate sensors (optodes) in order to determine Cr (VI). The optodes are made of optically transparent polymethacrylate matrix (PMM) with 1.5-diphenylcarbazide immobilized. The developed optode can be used in determination of the analytes using solid-phase spectrophotometry and calculating color coordinates as functions of absorbance spectra. Also color coordinates can be represented as basic color (e.g. RGB) data after the optode image digitizing. Then one can determine the content of an analyte in a sample by an appropriate color difference calculated on these coordinates. Experimental results of Cr (VI) determination show that the DCA characteristics of accuracy and precision are comparable with those of the solid phase spectrophotometry.

Keywords: Colorimetric sensor, optode, chromium (VI), transparent polymeric matrix, immobilized reagents, digital color analysis.

1. INTRODUCTION

Optical chemical sensors play an important part in industrial, environmental and clinical monitoring thanks to their low cost, possibility for miniaturization and great flexibility [1], [2]. Among different types of optical chemical sensors, colorimetric sensors are especially attractive because they recognize analytes through color change that allows obtaining the visually observed and easily measurable analytical signal [3], [4]. The analytical signal measurement can be carried out using not only standard spectrophotometric equipment, but also the naked eye without the use of an expensive equipment [6], [7]. Naturally, the naked eye techniques cannot be as accurate as spectrophotometry. That is why the visible color changes should be measured using different chromaticity coordinates (in RGB, XYZ, L*a*b*, and other systems) and parameters (total color difference (color variation) ΔE). Usually chromaticity parameters are calculated as functions of absorption or reflection spectra by means of computer programs intended for spectral data processing [5].

Nowadays, measurement of chromaticity parameters has become easier due to a wide use of scanners, digital photo and video cameras, etc. [5–7, 12]. An image of an optode is

captured and transferred to a computer and its color is interpreted using imaging software.

In the present work, an application of a kind of optical analytical method, digital color analysis (DCA), using colorimetric polymethacrylate sensors (optodes) in order to determine Cr (VI). The optodes are made of optically transparent polymethacrylate matrix (PMM) with 1.5-diphenylcarbazide immobilized. The developed optode has been used in determining Cr (VI) using solid-phase spectrophotometry and calculating color coordinates as functions of absorbance spectra. As an alternative approach, color coordinates can be represented by means of RGB data after the optode image digitizing. Subsequent determination of the content of Cr (VI) in a sample has been carried out on the base of calculating an appropriate color difference as a function of the RGB coordinates.

2. METHODS

2.1. Materials

The PMM is a specially created material containing functional groups which provide ability to extract both the reagent and determined substance [10]. Transparent 10 × 10 cm polymethacrylate plates, thickness (0.60 ± 0.04) mm, were prepared by the radical block polymerization of methacrylate and (alkyl)acrylates of alkaline (or alkaline earth) metals at the temperature 60–70 °C for 3–4 h. Then these plates were cut as 6.0 × 8.0 mm working platelets (weight ca. 0.05 g) intended for analyses.

All reagents were of analytical grade and used as purchased without further purification. Deionized and distilled water was used in all experiments. The work solutions of 0.025–0.200 % 1.5-diphenylcarbazide were prepared by dissolving precise loads in ethanol by heating at the water bath with the subsequent diluting by distilled water. The stock solutions of metals (1mg/ml) were prepared by dissolving precise loads of their salts in 0.01 M acids. The work standard solutions of the required concentration were prepared by dilution of the stock solution in the day of experiment. The required pH was adjusted using acid and alkali and controlled using an I-160 ionometer.

2.2. Procedure

The procedure of immobilization of 1.5-diphenylcarbazide (DPC) into the polymethacrylate matrix and inves-

tigations of the interaction of the immobilized DPC with Cr (VI) under different conditions are described in detail in [12]. Polymethacrylate matrix with the immobilized DPC was put into 50.0 mL of an analyzed solution of definite concentration of Cr (VI) at the pH \approx 0 and stirred for 15 min. After that absorption spectra of the PMM were measured. Then color coordinates X , Y and Z were calculated according to equations [8]:

$$X = k \sum_{380}^{780} \tau(\lambda) S(\lambda) \bar{x}_{10}(\lambda) \Delta\lambda, \quad (1)$$

$$Y = k \sum_{380}^{780} \tau(\lambda) S(\lambda) \bar{y}_{10}(\lambda) \Delta\lambda, \quad (2)$$

$$Z = k \sum_{380}^{780} \tau(\lambda) S(\lambda) \bar{z}_{10}(\lambda) \Delta\lambda, \quad (3)$$

where $k = \frac{100}{\sum_{380}^{780} S(\lambda) \bar{y}_{10}(\lambda) \Delta\lambda}$,

$\bar{x}_{10}(\lambda)$, $\bar{y}_{10}(\lambda)$, $\bar{z}_{10}(\lambda)$ are addition functions of CIE 1964 Supplementary Standard Observer, $\tau(\lambda)$ is transmittance of the PMM, $S(\lambda)$ is relative spectral power distribution of the CIE Standard Illuminant D65.

After that, chromaticity coordinates x , y , z were found according to equations:

$$x = X/(X + Y + Z), \quad (5)$$

$$y = Y/(X + Y + Z), \quad (6)$$

$$z = Z/(X + Y + Z), \quad (7)$$

where the condition $x + y + z = 1$ is valid.

Then the transition from XYZ to RGB system was made in accordance to the following equations:

$$r = 3.2405x - 1.5371y - 0.476z, \quad (8)$$

$$g = -0.9693x + 1.8760y + 0.041z, \quad (9)$$

$$b = 0.0556x - 0.2040y + 1.0572z. \quad (10)$$

The conversion from XYZ to CIE $L^*a^*b^*$ system was done as described by the following equations [9]:

$$L^* = \begin{cases} 116(Y/Y_n)^{1/3} - 16 & \text{if } Y/Y_n > 0.008856 \\ 903.3(Y/Y_n) & \text{if } Y/Y_n \leq 0.008856 \end{cases} \quad (11)$$

$$a^* = 500(f(Y/Y_n) - f(Y_n/Y_n)) \quad (12)$$

$$b^* = 200(f(Y/Y_n) - f(Y_n/Y_n)), \quad (13)$$

where $f(t) = \begin{cases} t^{1/3} & \text{if } t > 0.008856 \\ 7.787t + 16/116 & \text{if } t \leq 0.008856 \end{cases}$,

X_n , Y_n and Z_n – are values of coordinates of the white point of the system.

The total color difference for the chromaticity coordinates in XYZ, CIE $L^*a^*b^*$ and RGB color systems calculated from absorption spectra ($\Delta E_{\text{abs}}^{\text{XYZ}}$, $\Delta E_{\text{abs}}^{\text{Lab}}$ and $\Delta E_{\text{abs}}^{\text{RGB}}$) was estimated according to the equations:

$$\Delta E_{\text{abs}}^{\text{XYZ}} = (\Delta x^2 + \Delta y^2 + \Delta z^2)^{1/2} \quad (14)$$

$$\Delta E_{\text{abs}}^{\text{Lab}} = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2} \quad (15)$$

$$\Delta E_{\text{abs}}^{\text{RGB}} = (\Delta r^2 + \Delta g^2 + \Delta b^2)^{1/2} \quad (16)$$

where Δx , Δy , Δz ; ΔL^* , Δa^* , Δb^* and Δr , Δg , Δb are chromaticity coordinate changes in XYZ, CIE $L^*a^*b^*$ and RGB systems, correspondingly.

Besides, visible color changes of the PMM were estimated with digital imaging by means of a scanner and image processing software. The PMM image was captured and transferred to a computer and its color was interpreted using imaging software where the colorimetric data in RGB format were related to the concentration of the analyte.

The total color difference for the scanning images of the PMM (ΔE_{scan}) evaluated by means of scanner and software Photoshop CS was estimated according to equation:

$$\Delta E_{\text{scan}} = (\Delta R^2 + \Delta G^2 + \Delta B^2)^{1/2}, \quad (13)$$

where ΔR , ΔG and ΔB are changes coordinate of chromaticity in RGB system.

2.3. Apparatus

The absorption spectra and absorbencies of the PMM were recorded on the Shimadzu UV-mini-1240 and Spekol-21 spectrophotometers. A non-modified polymethacrylate matrix was used as the reference sample.

As the desktop scanner the Hewlett Packard Scanjet 4400 C was used. The personal computer was Pentium II (333 MHz). The software packages were used as follows: Photoshop CS for image collection and taking color intensities, Excel spreadsheet for general calculations and Origin 7.0 for plotting.

3. RESULTS AND DISCUSSION

The PMM with immobilized DPC after reaction with Cr (VI) had the red-violet color due to the formation of diphenylcarbazonate of chromium (III) complex. The absorption spectra of this complex in the PMM and scanned images of the PMM are presented in Fig. 1.

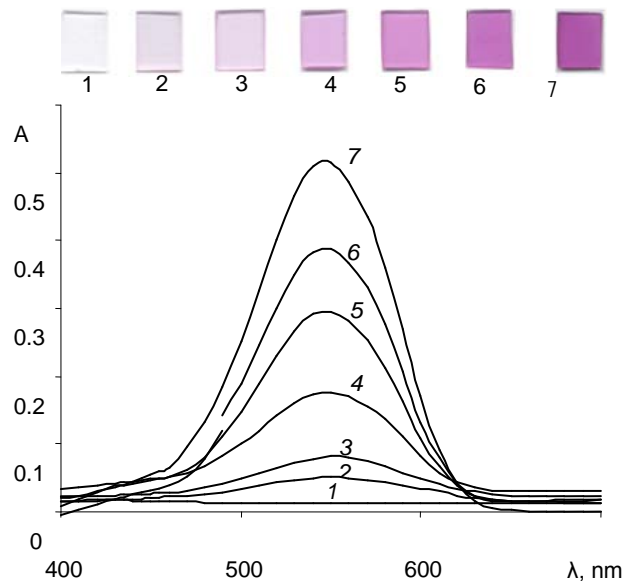


Fig. 1. Absorption spectrum of PMM with immobilized DPC after contact with Cr (VI) solution with concentration, $\text{mg}\cdot\text{L}^{-1}$: curve 1 – 0; curve 2 – 0.05; curve 3 – 0.10; curve 4 – 0.25; curve 5 – 0.50; curve 6 – 0.75; curve 7 – 1.00.

The absorption spectrum has a maximum at 545 nm. The absorption at the wavelength 545 nm was taken as the analytical signal for solid phase spectrophotometric determination of Cr (VI) which was explained in more detail in [12].

The concentration dependences for Cr (VI) were obtained by three different methods, namely: traditional solid phase spectrophotometry; the DCA with total color difference for the scanning images of the PMM; and the solid phase spectrophotometry with computing total color difference on the base of the chromaticity coordinates obtained of absorption spectra. The corresponding curves are shown in Fig. 2.

The concentration dependences for Cr (VI) are described by linear equations for all estimation methods of the visible color changes. In case of using of the total color difference calculated for scanning images of PMM, that is DCA, there

is observed the decreasing of the range of determined concentrations. Analytical performance for the linear equations of the color changes are presented in Table 1.

Table 1. Analytical performance of the Cr (VI) colorimetric sensor

Analytical signal	Calibration equation	R^1	RDC ² , mg·L ⁻¹
A_{545}	$A_{545} = 0.003 + 0.525 \cdot C_{Cr(VI)}$	0.998	0.05–1.00
ΔE_{abs}^{RGB}	$\Delta E = 0.002 + 0.167 \cdot C_{Cr(VI)}$	0.999	0.05–1.00
ΔE_{abs}^{Lab}	$\Delta E = 0.4 + 47.8 \cdot C_{Cr(VI)}$	0.999	0.05–1.00
ΔE_{abs}^{XYZ}	$\Delta E = 0.003 + 0.103 \cdot C_{Cr(VI)}$	0.998	0.05–1.00
ΔE_{scan}	$\Delta E = 7.1 + 176.6 \cdot C_{Cr(VI)}$	0.990	0.05–0.50

¹ Correlation coefficient

² Range of Determined Concentrations

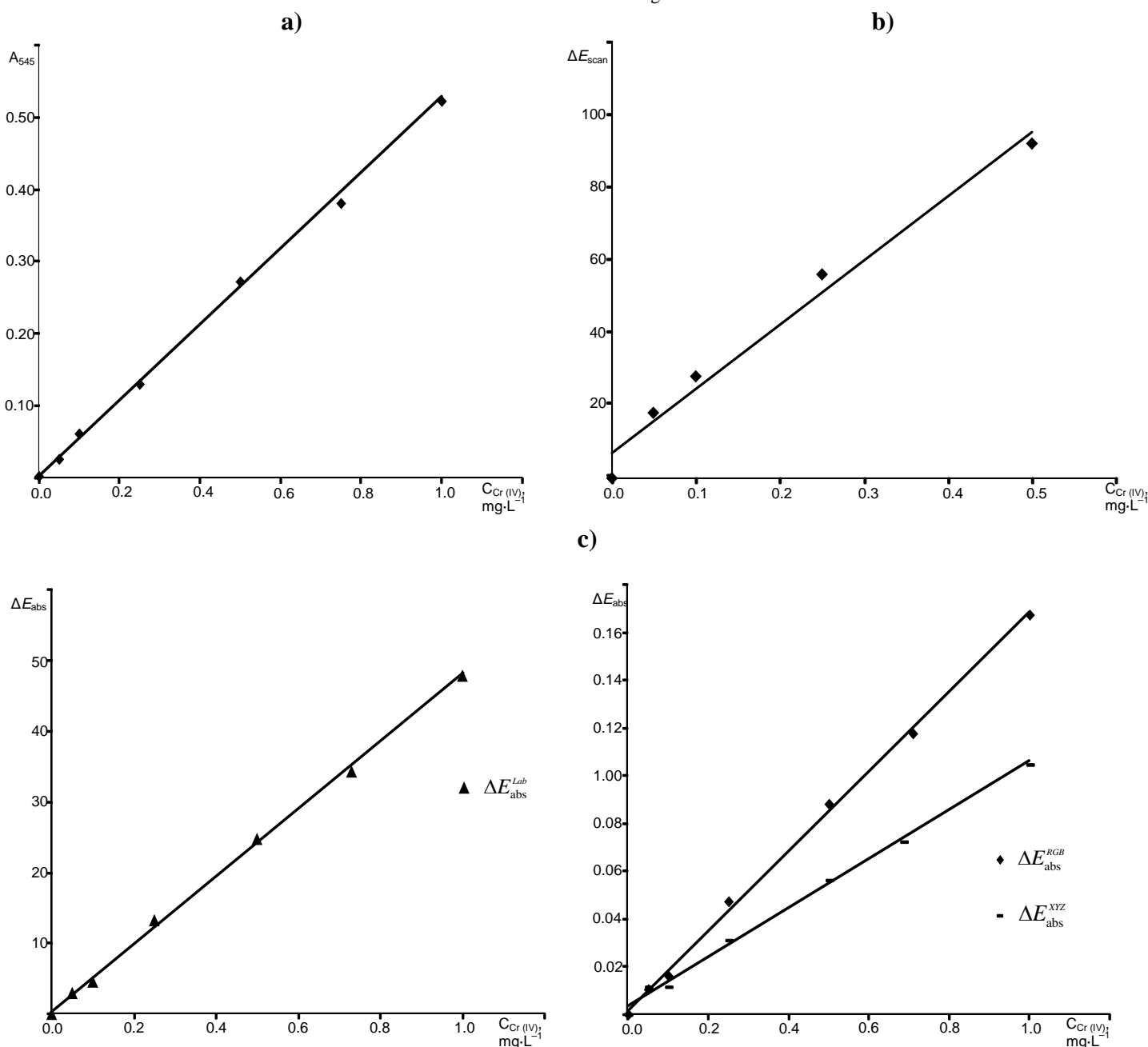


Fig.2 . Concentration dependence for determination of Cr (VI) obtained by different estimation methods of the visible color changes: a) traditional solid phase spectrophotometry, b) the DCA with total color difference computing for the scanning images of the optode and c) solid phase spectrophotometry with the total color difference for the chromaticity coordinates calculated from absorption spectra.

Table 2. Determination of Cr (VI) in tap water (sample volume $n = 5$, confidence level $P = 0.95$)

Techniques		Added, mg·L ⁻¹	Found, mg·L ⁻¹	RSD ¹ , %	Recovery, %
Solid phase spectrophotometry	A_{545}	0.070	0.065 ± 0.016	15	-7
		0.300	0.29 ± 0.03	7	-3
		0.600	0.601 ± 0.023	2	0.2
Color analysis	$\Delta E_{\text{abs}}^{\text{RGB}}$	0.070	0.066 ± 0.008	14	-6
		0.300	0.29 ± 0.02	8	-3
		0.600	0.63 ± 0.05	8	5
	$\Delta E_{\text{abs}}^{\text{Lab}}$	0.070	0.068 ± 0.008	14	-3
		0.300	0.28 ± 0.023	8	-5
		0.600	0.62 ± 0.05	8	3
	$\Delta E_{\text{abs}}^{\text{XYZ}}$	0.070	0.070 ± 0.013	21	0.2
		0.300	0.29 ± 0.03	12	-3
		0.600	0.63 ± 0.04	7	4
	ΔE_{scan}	0.070	0.071 ± 0.013	21	1
		0.300	0.311 ± 0.028	10	4

¹ Relative Standard Deviation

The accuracy and precision of Cr (VI) determination results were verified by the standard addition method with using drinking tap water (Table 2). One can see that the ΔE_{abs} and ΔE_{scan} characteristics of accuracy and precision are comparable with those of the solid phase spectrophotometry (A_{545}).

4. CONCLUSION

The proposed colorimetric sensor on the base of PMM with immobilized DPC can be used for determination of Cr (VI) by both solid-phase spectrophotometry and digital color analysis. In addition to above a scanner combined with a graphical editor can be used as a sensitive method of rapid laboratory analysis; it can be useful also to store color images for their further treatment when convenient.

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