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POLYMETHACRYLATE OPTICAL SENSORS FOR CHEMICAL ANALYSIS

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Abstract: Optical chemical sensors usually utilize immobilized reagents in a solid matrix usually in the form of a monolith or a thin film. The reagents immobilized into the sensor are responsible for the extraction of the analyte into the sensing material and generating an optical signal proportional to the change in the concentration of the analyte. In the work presented here we propose to use transparent polymethacrylate matrix (PMM) for physical immobilization of analytical reagents. The using of PMM allowed us to combine the capability of the solid phase to immobilize reagents without losing the matrix transparence and the capability of the reagents to participate in the analytical reaction with analytes accompanied by an optical effect.

Keywords: immobilized reagents, transparent polymeric matrix, optical sensor.

1. INTRODUCTION

Sensitive optical element is defining part of optical chemical sensor (optode) and is called transducer. It provides the molecular or ionic recognition by way of change its optical properties in dependence on the analyte. This optical signal may be absorption, emission, transmission, reflection of light by the transducer in the optode [1,2]. Absorption is no doubt the most frequently used detection technique in analytical laboratories due to its high flexibility for adaptation to a wide variety of analytical problems.

Standard way of manufacture of transducer is immobilization of analytical reagent on a suitable support matrix. The choice of a support matrix depends on parameters like permeability for the analyte, mechanical stability and suitability for reagent immobilization. As a support matrix different sorbents such as polymer matrix, cellulose and silica gel are used. By development of the sensor working on measurement absorption preference is given to the optical transparent polymer matrix because its absorbance is measured most simply. Thereby, researches are carrying out in the field of creation of transparent matrixes which preserve both analytical properties of immobilized reagents and optical properties of initial matrix.

Two general methods are widely applied for the immobilization of reagents in optodes. They are called physical and chemical immobilization. Physical immobilization may include adsorption, entrapment**,** encapsulation or electrostatic attraction between the reagent and polymer matrix. Chemical immobilization is finished by formation of covalent bonds between the reagent and support matrix. We are of the opinion that the most convenient way is physical immobilization, because these methods are simple and involve mild reaction conditions. As chemical immobilization is complexity and labour intensity of processes.

2. METHODS

Materials: PMM is the special created material containing functional groups which provide ability to extract both the reagent and determined substance. PMM in the form of transparent plate with surface 0.5 cm^2, thickness of (0.06 ÷ 0.08) cm and mass of 0.05 g was synthesized under laboratory conditions by radical block polymerization [3].

All reagents were of analytical grade and used as purchased without further purification. Deionized and distilled water was used in all experiments. The required pH was adjusted using acid and alkali and controlled using an I-160 ionometer.

Procedure: Immobilization of analytical reagents into a polymeric matrix has been carried out in a static mode. PMM soaked in water or water-organic solutions of reagents.

The quantity of sorbed PMM reagent is proportional to intensity of its painting and it depends on conditions of modification: pH, concentration of the reagent in solution (C_{reag}) and durations of processing. Optimal conditions for immobilization of reagents into PMM are resulted in Table 1.

The interactions of analytes with the reagents immobilized in PMM were studied by solid-phase spectrophotometry under batch conditions. For this purpose, PMM with an immobilized reagent was put into 50.0 mL of an analyte solution of different concentrations and pH and stirred for 5–30 min. After that absorption spectra or absorbance of PMM was measured.

Apparatus: The absorption spectra and absorbencies of PMM were recorded on the Evolution 600 spectrophotometer. An unmodified PMM was used as the reference sample.

3. RESULTS AND DISCUSSION

The reagents keep the analytical properties after immobilization into PMM. PMM does not influence upon spectroscopic and analytical properties of reagents. The absorption spectra of immobilized reagents and products of

Table 1. Conditions for immobilization of reagents into PMM

Reagent*	Solvent	C_{reag}, mol/L	pH	Contact time, min	Concentration of reagent into PMM, μmol/g
PAN	water –ethanol	0,00025	4 - 9	5,0	1,0±0,1
DThZ	CCl_4	0,002	-	0,5	1,4±0,3
	NaOH	0,002	10	1,0	2,2±0,2
2,2'-dip	water	0,015	6-7	5,0	45±5
1,10-phen	water	0,015	6-7	5,0	50±5
DDTC	water	0,1	5-6	15	170±40

* PAN – 1-(2-pyridylazo)-2-naphtol, DThZ – dithizone, 2, 2'-dip – 2, 2'-dipyridyl, 1, 10-phen – 1, 10-phenantroline, DDTC – diethyldithiocarbaminate.

analytical reaction in PMM after contact with determined substance coincide both in the solution and in the matrix.

For example, the complexing reagents keep the analytical properties after immobilization into PMM. PMM with immobilized complexing reagents changes color in water solutions after contact with determined metal owing to formation of complexes into polymeric matrix. Spectrophotometric characteristics of immobilized reagents and their complexes with metals ions are investigated. The absorption spectra of complexes inside PMM are similar to obtained in solutions. That confirms the formation of complexes with identical structure both into a polymeric matrix and solutions. Formation of metals complexes with reagents into PMM depends on pH of aqueous solution. The optimal values pH (pH_{opt}) of metals solutions for complexing with immobilized into PMM reagents and characteristics of formed into PMM complexes are resulted in Table 2. These characteristics are practically similar to those of compounds formed in solutions. This leads us to the conclusion that the properties of the reagents in the solution and in the polymer matrix are similar. Thus, the well-known conditions of the corresponding reactions in the solution can be used for the reaction in the polymer.

Furthermore, immobilized reagents and their complexes with metals do not affect the transparency of PMM. That allows spending the direct measurement of optical characteristics of a sensitive element with high accuracy.

Techniques of solid phase spectrophotometric are developed on the basis of the obtained results.

The optical sensitive membranes for the determination of analytes in various objects using spectrophotometry are presented in Table 3. The relative standard deviation for these determinations was in the range of 3–20% depending on analyte concentration.

Same samples of PMM with reagents after contact with determined metals are showed in Fig. 1.

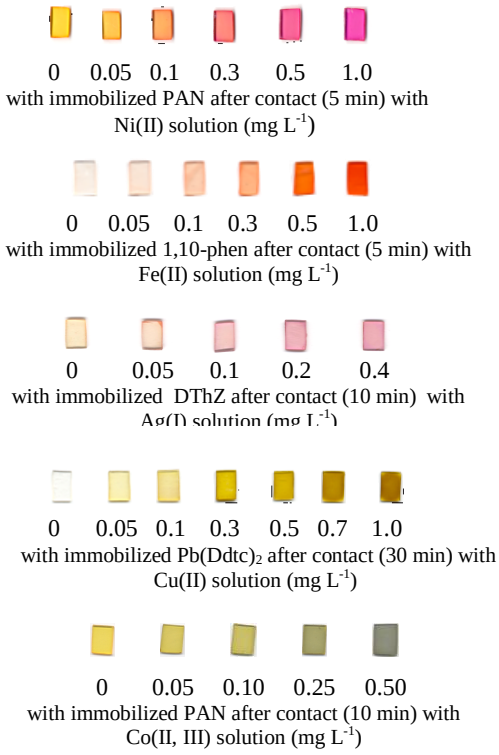

Fig. 1. The scanned images of the PMM with immobilized reagents after contact with metal ions solutions

Table 2. Characteristics of metals complexes into PMM

Reagent	Metal	Color of complex into PMM	λ_{max}, nm	Ratio Me : R in complex	pH_{opt}
PAN	Cu (II)	Violet	555	1:2	5-6
	Zn (II)	Red	515, 545		5-8
	Cd (II)	Red	520, 545		5-7
	Pb (II)	Red	540		5-8
	Mn (II)	Crimson	515, 540		6-7
	Ni (II)	Crimson	525, 565		4-7
	Co (II, III)	Green	580, 620		4-11
DThZ	Hg (II)	Orange	485	1:2	0-3
	Ag (I)	Red-violet	520	2:1	5-11
2,2'-dip	Fe (II)	Red	520	1:3	4,5-5,5
1,10-phen		Orange	510		4,5-5,5
DDTC	Cu (II)	Yellow-brown	430	1:2	4-8

Table 3. Optical sensitive membranes on the base of PMM with immobilized reagents

Immobilized reagent	Analyte	RDC*, mg·L^{-1}	Objects of analysis
diethyldithiocarbamate - Pb(II) complex	Cu (II)	0,02-1,00	pharmaceutical preparations, water
1-(2-pyridylazo)-2-naphtol	Co (II, III)	0,03-0,50	pharmaceutical preparations, water
dithizone	Ag (I)	0,04-0,80	pharmaceutical preparations, mineral water
2,2'-dipyridyl	Fe (II, III)	0,2-5,0	drinking water
1,10-phenanthroline		0,2-5,0	
2,6-dichlorophenolindophenol	Ascorbic acid	10-100	food products, juice
Fe(III) - 1,10-phenanthroline	Total antioxidant activity	10-30**	wine, black and green tea, drinks
diphenylcarbazone - Hg (II) complex	Chloride	50-1800	mineral water
alizarine red - Zr (IV) complex	Fluoride	0,2-5,0	mineral water, toothpaste
Griss reagent	Nitrites	0,9-3,0	water, soil
dithizone	Se (IV)	0,09-0.5	pharmaceutical preparations

*RDC – the range of determined concentrations; ** The antioxidant activity was expressed as mg L^{-1} of ascorbic acid

We proposed to estimate the intensity of color in the form of colorimetric characteristics with application of computer programs of digital processing of the scanned image (new kind of optical analytical method – digital color analysis, DCA [4]). The scanned images of transducers on basis of PMM were analyzed on the clarity in coordinates R, G, B with Adobe Photoshop. The possibilities of using a scanner as an analytical instrument in working with PMM color scales were exemplified by the determination of Co (II, III), Ag (I) and Cu (II). It was found that an increase in the concentration of the test component, accompanied by an increase in the intensity of the sorbent color, results in a decrease in the clarity of the R, G, and B channels of the color image. As an example, the figure 1 shows the dependences of the clarity of R, G, and B channels on the concentration of Cu (II).

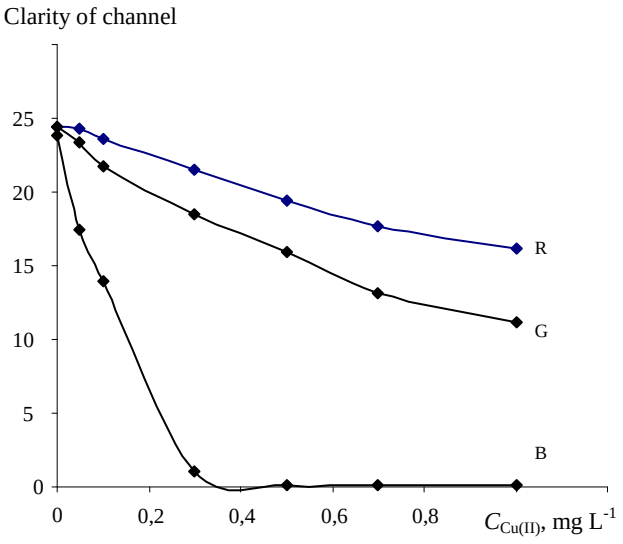

Fig.2. Clarity of R, G, B channels of a color image of the color scales as a function of concentration of Cu (II)

For each studied color scale, we selected the brightest channel, which was chosen as the analytical signal. As expected, for the yellow-brown colored samples of color scales for the determination of Cu (II) having absorption maxima 430 nm in the blue region (Table 2), the brightest channel is blue (B). In contrast, for green-colored samples PMM with immobilized PAN after contact with Co (II, III) solution, which absorb light in the red region of spectra (620 nm), the brightest channel is the red (R); for the red-violet colored samples of color scales for the determination of Ag (I), the brightest channel is green (G). Table 4 summarizes the color channels selected for the determination of substances and the parameters of calibration equations. The limit of detection were calculated according to the 3s-test.

Table 4. Calibration equations as clarity vs. concentration of the test component (mg·L^{-1})

Test component	Color channel	Calibration equation	R^2
Cu (II)	B	B=224-748·c_{Cu}	0,987
Ag (I)	G	G=220-212 c_{Ag}	0,998
Co (II, III)	R	G=256-213 c_{Co}	0,950

We compared the DCA and the solid phase spectrophotometry for determined components (Table 5). A comparison of the metrological parameters of the procedures for the determination of analytes shows that the selected components can be determinated with the use of a scanner and image-processing software with practically the same sensitivity as with the use solid phase spectrophotometry [5, 6].

Table 5. Range of determined concentrations (RDC, mg·L^{-1}) and limit of detection (LOD, mg·L^{-1}) of the test component

Test component	Solid phase spectrophotometry		Digital color analysis	
	RDC	LOD	RDC	LOD
Cu (II)	0,02-1,00	0,015	0,02-0,30	0,010
Ag (I)	0,04-0,80	0,03	0,02- 0,80	0,02
Co (II, III)	0,03-0,50	0,03	0,05-0,25	0,07

The accuracy and precision of the results of the determination of the test components were verified by the standard addition method (Table 6). A comparison of the determination methods shows a good accuracy and precision of the determination of Cu (II) and Co (II, III) in water using a scanner and image-processing software.

Table 6. Determination of Cu(II) and Co (II, III) in tap water (*n*=5, *P*=0,95)

Test component	Objects	Added, mg L^{-1}	Techniques			
			Solid phase spectrophotometry		Digital color analysis	
			Found, mg·L^{-1}	s_r	Found, mg·L^{-1}	s_r
Cu (II)	sample-1	-	0,03±0.02	0,41	<0.02	0,50
		0,30	0,34±0.05	0,13	0,29 ±0,07	0,10
	sample-2*	-	1,02±0.13	0,10	1,09 ±0,12	0,09
		0,30	1,26±0.17	0,11	1,32±0,09	0,12
Co (II, III)	-	0,25	0,21±0,02	0,04	0,25±0,05	0,08

*- Estimation of effect of the material (copper pipes) contacting to water to its quality

The results of silver determination in in the antiseptic cream Argosulfan® (Sulfathiazole silver) are presented in Table 7. These are comparable with the accuracy and precision of solid phase spectrophotometry.

Table 7. Determination of silver in Argosulfan (*n*=5, *P*=0,95)

Techniques	Found, mg·g^{-1}	σ_r, %	Official certificate data, mg·g^{-1}
Digital color analysis	17,3±2,6	14,1	20
Solid phase spectrophotometry	19,0±2,5	10,7	

4. CONCLUSION

The PMM has not an effect on analytical properties of immobilized reagents and it can be used by a basis for development of optical recognition elements.

The advantages of using PMM is combination the capability of the solid phase to immobilize reagents without losing the matrix transparence and the capability of the reagents to participate in the analytical reaction with analytes accompanied by an optical effect. That allows spending the direct measurement of optical characteristics of a sensitive element with high accuracy.

The proposed sensitive optical membranes can be used for the determination of various substances by solid-phase spectrophotometry and digital color analysis.

5. ACKNOWLEDGMENTS

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6. REFERENCES

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