

Colorimetric Polymethacrylate Sensor

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Keywords: colorimetric sensor, transparent polymeric matrix, immobilized reagents, solid-phase spectrophotometry, naked-eye determination

Abstract. The paper describes a new colorimetric sensor. The colorimetric sensors were made of optically transparent polymethacrylate matrix with physically immobilized analytical reagent which is responsible for the extraction of the analyte into the sensing material and changing its color. The developed colorimetric sensor can be used in determination of various analytes using both solid-phase spectrophotometer and naked eye.

Introduction

Optical chemical sensors play an important role in industrial, environmental and clinical monitoring as a result of their low cost, possibility for miniaturization and great flexibility [1-3]. Among different types of optical sensor, colorimetric sensors are especially attractive because they recognize analytes through color change that allows obtaining the visually observed and easily measurable analytical signal [4]. The measurement of the analytical signal can be carried out using not only standard spectrophotometric equipment, but some modern engineering solutions like portable fiber optic spectrometer connected to a laptop or cell phone and also the naked eye without the use of expensive equipment.

Colorimetric sensors usually utilize reagents immobilized in a solid matrix usually in the form of a monolith or a thin film. The immobilized into the matrix reagents are responsible for the extraction of the analyte into the sensing material and generating an optical signal proportional to change in the analyte concentration. Choice of a support matrix depends on various parameters like permeability for the analyte, mechanical stability and suitability for reagent immobilization. As a support matrix, different sorbents are applied, such as polymer matrix, cellulose and silica gel. In the course of the colorimetric sensor development, preference was given to the optical transparent polymer matrix due to its absorbance can be measured in most ease way. Another advantages of the polymeric materials are its high mechanical strength, chemical resistance, processability and possibility to be incorporated into measuring instrument [5-7]. Thereby, many scientific groups carry out researches aimed on creation of transparent matrixes able to preserve both analytical properties of immobilized reagents and optical properties of an initial matrix. In this paper, it is proposed to use transparent polymethacrylate matrix (PMM) for physical immobilization of analytical reagents. This allows to combine both the solid phase capability to immobilize reagents without losing the matrix transparency and the reagents capability to participate in the analytical reaction with analytes accompanied by an optical effect [8].

Methods

Materials. The PMM is a specially 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 $(0.06 \div 0.08) \text{ cm}$ and mass of 0.05 g was synthesized under laboratory conditions by radical block polymerization [8].

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 (sulfuric acid, nitric acid, phosphoric acid) and sodium hydroxide.

Procedure. Reagents were immobilized into PMM by adsorption from a solution in the batch mode. 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 [9, 10]. Optimal conditions for immobilization of some reagents into PMM are resulted in Table 1.

Table 1. Conditions for immobilization of reagents into PMM

Reagent	Solvent	C_{reag} , [g·L ⁻¹]	pH	Contact time, [min]
1-(2-pyridylazo)-2-naphtol	water – ethanol	0.06	4 - 9	5.0
dithizone	chloroform	0.50	-	0.5
	water-soap solution		10	1.0
2,2'-dipyridyl	water	2.0	6-7	5.0
1,10-phenanthroline	water	2.0	6-7	5.0
diethyldithiocarbamate	water	20.0	5-6	15
2,6-dichlorophenolindophenol	water	0.1	6.7	5

The interactions of analytes with the immobilized in PMM reagents 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. Absorption spectra and absorbance of PMM matrix were recorded on Evolution 600 spectrophotometer (Thermo Fisher Scientific Inc., USA) against a polymer plate prepared under the same conditions, without reagents. The pH values were measured by I-160 ion meter (NPO "Izmeritelnaya tekhnika", Russia) with a glass pH-selective electrode.

Results and discussion

The reagents keep the analytical properties after immobilization into PMM. PMM does not influence upon optical and analytical properties of reagents. The absorption spectra of immobilized reagents and products of 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 confirm the formation of complexes with identical structure both into a polymeric matrix and solutions [9]. 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.

Table 2. Characteristics of metal complexes in PMM

Reagent	Metal	Color of complex into PMM	λ_{\max} , [nm]	Ratio Me : R in complex	pH _{opt}
1-(2-pyridylazo)-2-naphthol	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
dithizone	Hg (II)	Orange	485	1:2	0-3
	Ag (I)	Red-violet	520	2:1	5-11
2,2'-dipyridyl	Fe (II)	Red	520	1:3	4.5-5.5
1,10-phenanthroline		Orange	510		4.5-5.5
diethyldithiocarbamate	Cu (II)	Yellow-brown	430	1:2	4-8

We investigated the raise of selectivity of reagents by the example of DThZ and DDTC at their use in the form of complexes with metals. This way is based on exchange reaction of one metal ion on another. The metals ions capable to an exchange were chose accordantly by literature data so that the determined metal ion formed stronger complex than the expelled from this complex metal ion. The Pb(II)-diethyldithiocarbamate (Pb(Ddte)₂) is chosen as reagent for determination of Cu(II) and Cu(II)-dithizonate (CuDz) is chosen for determination of Hg (II). The exchange reaction interacting Hg(II) with immobilized into PMM the CuDz is carried out with formation of keto-complex Hg(Dz)₂ at pH of solution Hg(II) equal 1-2 [11]. Replacement Pb(II) in Pb(Ddte)₂ on Cu(II) into PMM occurs in the pH interval 4.5-6.5. The immobilization of Pb(Ddte)₂ and CuDz into PMM was proceeded in two stages. First, the initial sample was exposed to the solution of reagent (Ddte or DThZ); then, the plate modified by the reagent was kept in solution of metal ions (Pb(II) or Cu(II)).

In addition to the complexation reactions we studied the possibility of oxidation-reduction reactions in the polymethacrylate matrix as exemplified by 2,6-dichlorophenolindophenol (DCIP) [10]. The formal redox potentials DCIP in solution and in the immobilized state as functions of the pH of the solution value are presented in Table 3. As the results shows oxidative activity of the immobilized DCIP decreases with respect to its activity in the solution because of diffusion and steric hindrances. However, the stability of the indicator in the PMM increased, which allowed the measurement of the formal potential of the immobilized DCIP at pH < 4. Therefore, the immobilization of DCIP on the polymethacrylate matrix ensures the determination of reductants in more acidic media that is useful in particular regarding the analysis of ascorbic acid due to increase its stability in acidic media.

Table 3. Formal redox potentials (E^0 , mV) of DCIP in aqueous solution (I) and on the polymethacrylate matrix (II)

pH	2.0	3.0	4.0	5.0	6.0
I	–	–	466 ± 4	394 ± 6	332 ± 10
II	451 ± 21	420 ± 14	385 ± 11	356 ± 10	330 ± 13

We examined the feasibility of using a polymethacrylate matrix (PMM) with an immobilized Fe(III) – o-phenanthroline system (Fe(III)-phen) for the assessment of antioxidant activity. The immobilization of Fe(III)-phen into PMM consisted of two stages. First, the starting sample was kept in a mixture of a 0.5% solution of o-phenanthroline in the acetate buffer solution for 5 min followed by an aqueous solution of Fe(III) (0.3 mg/ml) for 5 min. The polymer plate after the adsorption of the reagents remained colorless and transparent. As an antioxidant for the study we

selected the most frequently encountered in real objects antioxidant phenolic nature such as quercetin, tannin, rutin, gallic acid, catechin, luteolin, and non-phenolic nature - ascorbic acid and cysteine. The concentration of the antioxidant was quantified through the measurement of the absorbance changes at 510 nm of PMM with the immobilized Fe(III)-phen associated with the formation of the highly colored Fe(II)-phen chelate as a result of reaction with antioxidants. Fig. 1 presents absorption spectra of PMM–Fe(III)-phen after its contact with antioxidant sample solution (pH – 3,0–3,5). Under optimum conditions linear calibration curves were obtained for antioxidant concentrations ranging from 10 to 30 g·L⁻¹. Ascorbic acid was chosen as a standard for the antioxidant activity due to its reducing properties and availability.

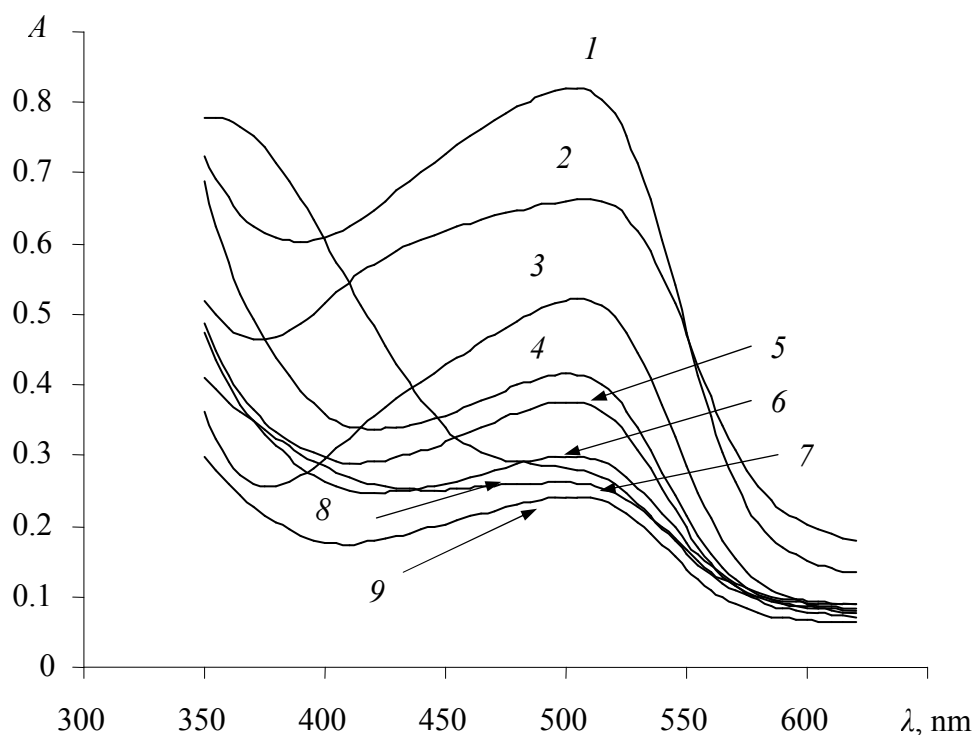


Fig 1. Absorption spectra PMM–Fe(III)-phen after its contact with antioxidant sample solution:

1 - gallic acid, 2 - quercetin, 3 - ascorbic acid, 4 - catechin, 5 - dihydroquercetin, 6 - tannin, 7 - luteolin, 8 - rutin, 9 - cysteine

Thus, the investigations performed in this work showed that the polymethacrylate matrix with immobilized reagents can be used as an optical membrane for the determination of analytes in various objects. The optical sensitive membranes for the determination of analytes using spectrophotometry are presented in Table 4. The relative standard deviation for these determinations was in the range of 3–20% depending on analyte concentration.

Also determination of analytes using PMM with immobilized reagents can be carried out by the naked eye. Naturally, the naked eye techniques cannot be as accurate as spectrophotometry. In order to improve the accuracy and sensitivity of the naked eye method, visible color changes can be measured by using a camera, phone or scanner [15-17]. A colorimetric sensor image is captured and transferred to a computer and the color is interpreted using an imaging software. The examples of scanned images of PMM with immobilized reagents after contact with metals are shown in Fig. 3. The scanned images of PMM can be analyzed on the intensity in coordinates RGB with Adobe Photoshop related to the concentration of the analyte. We compared the digital image processing and the solid phase spectrophotometry for determined analytes [18]. A comparison of the metrological parameters of the procedures for the determination shows that analytes can be

determined with the use of a scanner and image-processing software with practically the same sensitivity as with the use solid phase spectrophotometry.

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	
dithizone	Ag (I)	0.04-0.80	
	Se (IV)	0.09-0.50	
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

*RDC is the range of determined concentrations

** The antioxidant activity is expressed as mg·L⁻¹ of ascorbic acid

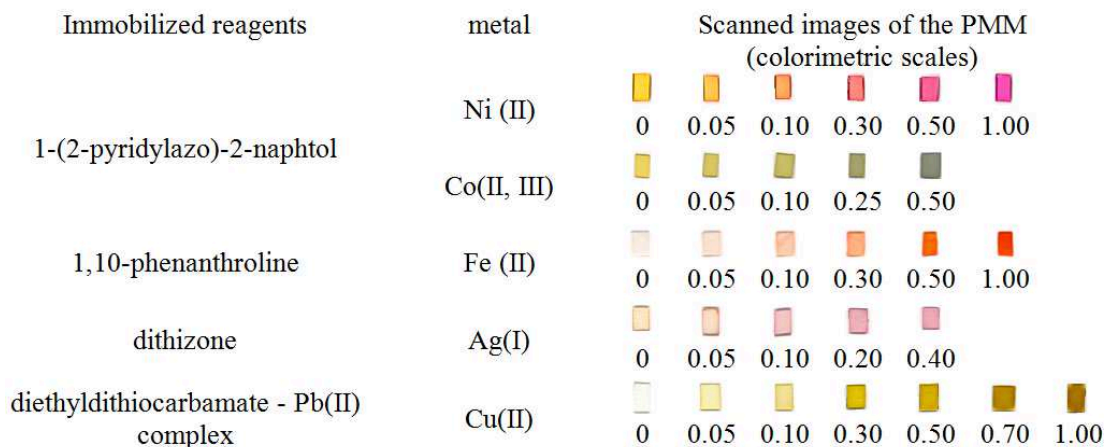


Fig. 3. The scanned images of the PMM with immobilized reagents after contact with metal ions solutions [mg·L⁻¹]

Conclusion

The aim of this paper is to present an easy-to-use optical-sensing material. The proposed colorimetric sensor on the base of PMM can be used for determination of various analytes by both spectrophotometry and naked-eye without the use of expensive equipment. The analysis with application of the presented sensors is simplicity, rapid, sensitive and inexpensive.

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