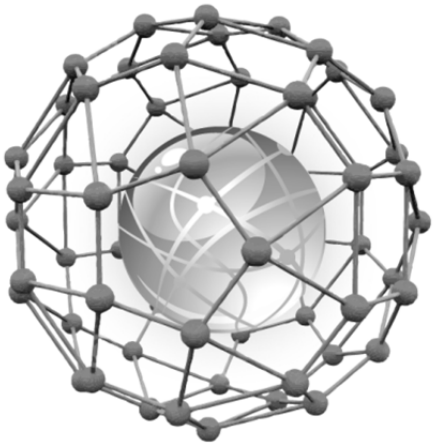
МИНИСТЕРСТВО ОБРАЗОВАНИЯ И НАУКИ РОССИЙСКОЙ ФЕДЕРАЦИИ
НАЦИОНАЛЬНЫЙ ИССЛЕДОВАТЕЛЬСКИЙ
ТОМСКИЙ ГОСУДАРСТВЕННЫЙ УНИВЕРСИТЕТ
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ПОЛИФУНКЦИОНАЛЬНЫЕ ХИМИЧЕСКИЕ МАТЕРИАЛЫ И ТЕХНОЛОГИИ

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Генистеин в условиях ВЭЖХ разделения, приведенных выше, обнаруживает пик со временем удерживания 10,73 мин. В результате окисления этот пик уширяется с переднего фронта, из чего можно сделать вывод об образовании более полярного соединения, время удерживания которого незначительно сокращается в условиях обращено-фазовой ВЭЖХ.

В условиях MS с интерфейсом ESI на отрицательных ионах нативный генистеин формирует сигнал с m/z = 269, соответствующий депротонированной молекуле $[M–H]^-$. В режиме MS/MS родительский молекулярный ион m/z = 269 генерирует фрагменты с m/z = 241, 151, 135, 133,107, 105, 91. На рис. 1 приведена схема и продукты фрагментации молекулярного иона по связям пропанового цикла.

Продукт окисления генистеина с m/z = 285 был анализирован в режиме MS/MS, спектр которого показал наличие осколочных ионов с m/z = 257, 229, 151, 149, 133, 121 (рис.2).

Сопоставление продуктов фрагментации молекулярных ионов исходной и окисленной формы генистеина позволяет установить местоположение дополнительной гидроксильной группы в молекуле (кольцо В), а приведённый пример иллюстрирует саму возможность применения ВЭЖХ-МС/МС для предварительного установления структуры соединения.

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COLORIMETRIC SENSORS FOR DETERMINATION OF HEAVY METAL IONS

Ekaterina S. Krylova, student, National Research Tomsk State University, Chemistry Department, 36, Lenina Avenue, Tomsk, 634050, Russia, E-mail: ekaterinakrylova93@gmail.com
Dmitry A. Fedan, student, National Research Tomsk State University, Chemistry Department, 36, Lenina Avenue, Tomsk, 634050, Russia, E-mail: dmitry061093@mail.ru
Nataliya A. Gavrilenko, Ph.D., Associate Professor of Department of Analytical Chemistry, National Research Tomsk State University, Chemistry Department, 36, Lenina Avenue, Tomsk, 634050, Russia, E-mail: gavrilenko@mail.tsu.ru
Nadezhda V. Saranchina, Ph.D., Associate Professor of Department of Ecology and Basic Safety, National Research Tomsk Polytechnic University, Institute of Non-Destructive Testing, 33, Lenina Avenue, Tomsk, 634050, Russia, E-mail: saranchina@mail.tsu.ru
Gennady M. Mokrousov, D.Sc., Professor of Department of Analytical Chemistry, National Research Tomsk State University, Chemistry Department, 36, Lenina Avenue, Tomsk, 634050, Russia, E-mail: mgm@vtomske.ru

The paper describes a new colorimetric sensor for determination of heavy metals ions. The colorimetric sensors were made of optically transparent polymethacrylate matrix (PMM) 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 heavy metals ions using both solid-phase spectrophotometer and naked eye.

Key words: colorimetric sensor, transparent polymeric matrix, immobilized reagents, heavy metals

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]. 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 [2, 3]. 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. In the work presented here, we propose to use transparent PMM with physical immobilized analytical reagents as the sensing phase in an colorimetric sensor for heavy metal ions. This allows to combine both the solid phase capability to immobilize reagents without losing the matrix transparence and the reagents capability to participate in the analytical reaction with analytes accompanied by an optical effect [4].

Methods. 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 (0,06–0,08) cm and mass of 0,05 g was synthesized under laboratory conditions by radical block polymerization [4]. 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. Reagents were immobilized into PMM by adsorption from a solution in the batch mode. 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. Absorption spectra and absorbance of PMM matrix were recorded on UNICO 2800 against a polymer plate prepared under the same conditions, without reagents. The pH values were measured by I–160 ion meter with a glass pH-selective electrode.

Results. 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. 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 tabl. 1. 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 1

Characteristics of metal complexes in PMM

Reagent	Metal	Color of complex into PMM	λmax, nm	Ratio Me : R in complex	pH_{opt}
1-(2-pyridylazo)-2-naphtol	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
	Pd(II)	Green	615, 665	1:1	0–4
dithizone	Hg(II)	Orange	485	1:2	0–3
	Ag(I)	Red–violet	520	2:1	5–11
	Pd(II)	Brown	450	1:2	2–6
		Violet	530	1:1	0–1
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
diphenylcarbazide	Cr(VI)	Red–violet	545	1:1 diphenylcarba-zonate Cr(III)	0–1

Table 2

Optical sensitive membranes on the base of PMM with immobilized reagents

Analyte	Immobilized reagent	RDC*, $mg \cdot L^{-1}$	Objects of analysis
Cu(II)	diethyldithiocarbamate – Pb(II) complex	0,02–1,00	pharmaceutical preparations, water
Co(II, III)	1-(2-pyridylazo)-2-naphtol	0,03–0,50	
Ag(I)	dithizone	0,04–0,80	
Se(IV)		0,09–0,50	
Pd(II)	1-(2-pyridylazo)-2-naphtol	0,1–1,0	environmental, waste and drinking water
	dithizone		
Fe(II, III)	2,2’-dipyridyl	0,2–5,0	
	1,10-phenanthroline		
Cr(VI)	diphenylcarbazide	0,01–0,50	

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 ($Pb(Ddtc)_2$) 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. Replacement Pb(II) in $Pb(Ddtc)_2$ on Cu(II) into PMM occurs in the pH interval 4,5–6,5. The immobilization of $Pb(Ddtc)_2$ and CuDz into PMM was proceeded in two stages. First, the initial sample was exposed to the solution of reagent (Ddtc or DThZ); then, the plate modified by the reagent was kept in solution of metal ions (Pb(II) or Cu(II)).

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 sensing phase with high accuracy. The sensing phase in the proposed colorimetric sensor for the determination of heavy metals in various objects using spectrophotometry are presented in tabl. 2. The relative standard deviation for these determinations was in the range of 3–20 % depending on analyte concentration.

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 heavy metals without the use of expensive equipment. The analysis with application of the presented sensors is simplicity, rapid, sensitive and inexpensive.

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ХИМИКО-АНАЛИТИЧЕСКИЙ КОНТРОЛЬ БИОСУБСТРАТОВ ЧЕЛОВЕКА ДЛЯ ДИАГНОСТИКИ ЗАБОЛЕВАНИЙ И ОЦЕНКИ СРЕДЫ ОБИТАНИЯ

Кускова Ирина Сергеевна, аспирант кафедры аналитической химии,
Национальный исследовательский Томский государственный университет, химический факультет,
634050, Россия, г. Томск, пр. Ленина, 36, E-mail: kuskova.i@mail.ru
Отмахов Владимир Ильич, д-р техн. наук, профессор кафедры аналитической химии,
Национальный исследовательский Томский государственный университет, химический факультет,
634050, Россия, г. Томск, пр. Ленина, 36, E-mail: otmahov2004@mail.ru
Петрова Елена Васильевна, канд. хим. наук, доцент кафедры аналитической химии,
Национальный исследовательский Томский государственный университет, химический факультет,
634050, Россия, г. Томск, пр. Ленина, 36, E-mail: elena1207@sibmail.com

Одним из условий нормального функционирования организма является стабильность его химического состава. Изменения содержания химических элементов, обусловленные экологическими, климатогеографическими и др. факторами, могут приводить к патологическим отклонениям здоровья человека [1]. В современной практике диагностики макро- и микроэлементов в организме человека существуют методы их определения в цельной крови, моче, волосах, слюне, зубном дентине и костной ткани. Среди указанных биологических субстратов волосы, как объект исследования, более предпочтительны. Их отличает довольно постоянный химический состав (благодаря кератиновой наружной оболочке), высокая концентрация микроэлементов вследствие связывания с тиоловыми группами цистеина и накопления, малая зависимость от систем, регулирующих гомеостаз (восстановление утраченного равновесия), возможность неограниченного хранение без специального оборудования, неинвазивность при отборе проб и легкость удаления внешних загрязнений.

Актуальность работы обусловлена дефицитом экспрессных, метрологически аттестованных методик анализа биосубстратов человека, в том числе волос.

Цель работы заключалась в разработке методики количественного определения макро- и микроэлементов в волосах пациентов с целью диагностики различных заболеваний и выявления клинико-лабораторных корреляций.