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Uranyl ion-selective optical test strip

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ABSTRACT

A novel, optical sensor, test strip has been developed for the spectrophotometric determination of trace amounts of uranyl ions, UO_2^{2+}, based on immobilization of C.I. Mordant Blue 29 (Chromazurol S)/cetyl *N*,*N*,*N*-trimethyl ammonium bromide ion pair on a triacetyl cellulose membrane. Optimization of the sensor for the detection of low levels of uranyl ion is described. The test strip responded linearly to uranyl ions between 3.0×10^{-7} and 6.0×10^{-5} mol L^{-1}; the reproducibility of the sensor at a medium level of UO_2^{2+} activity was ±0.55%. The optical sensor can be regenerated using 0.01 mol L^{-1} HCl or 0.01 mol L^{-1} NaF solution after 10 min. The developed test strip was used in the determination of UO_2^{2+} in ground water samples.

1. Introduction

Due to dangerous and harmful properties of uranium for the health of human beings, the determination of uranium is very important [1]. The optical methods for the determination of uranium are inductively coupled plasma atomic emission spectrometry (ICP-AES) [2], inductively coupled plasma mass spectrometry (ICP-MS) [3] and UV–vis spectrophotometry using chemical reagents such as Arsenazo III [4,5]. Although these methods have good sensitivity, they require expensive instruments, well controlled experimental conditions and profound sample masking or time consuming and cannot be used for screening assay. Optical chemical sensors have drawn much attention in analytical chemistry, because of some advantages such as easy fabrication, good sensitivity, selectivity and low cost [6–11]. Different strategies have been used to develop optical sensors for some target ions. Optical or visual test strips allow the simple detection of analyte by the naked eye, or by a portable spectrophotometer without any specific pretreatment [12].

Many of the reported optical sensors for uranyl ion determination are based on incorporating the dye into a poly(vinyl chloride) matrix [13–15]. These membranes have a main shortcoming in leakage of the dye into the aqueous solution in contact with them. The immobilization of the organic dye can prevent this leaking. Recently, a few works on the development of the optical sensor for uranyl ion sensing have been reported based on immobilization of Arsenazo III on the membranes such as polyacrylonitrile [16], polyamide materials [17] and Nafion [18]. Safavi and Oehme [19,20] used the lipophilized dye molecules by synthesis of a lipophilic derivative of an indicator and immobilization in the acetate cellulose and Nafion matrices, respectively. Cellulose is an ideal support for ion sensing, because of its hydrophilicity and ion permeability.

Arsenazo III is a common chromogenic reagent for the spectrophotometric determination of uranium but the method is time consuming and the non-specific nature of Arsenazo III complexation can lead to interferences from the high concentration of metals ions [21]. Chromazurol S (C.I. Mordant Blue 29; CAS) has gained importance in the spectrophotometric determination of uranium [22]. In the presence of cationic surfactant such as cetyl *N*,*N*,*N*-trimethyl ammonium bromide (CTAB), a significant increase in sensitivity is observed. The molar absorptivity of the UO_2^{2+}–CAS complex in a micelle solution of CTAB is comparable to, or less than, that of the uranium–Arsenazo III complex, but the interferences from coexisting elements including thorium can be avoided by masking with EDTA.

The test strip proposed here is based on the use of a chromogenic compound, CAS, which was lipophilized by ion pairing with CTAB and immobilization of the ion pair CAS–CTAB (Fig. 1) on triacetyl cellulose membrane. Upon dipping the test strip into a pH-buffered uranyl solution, the color of the membrane changed from

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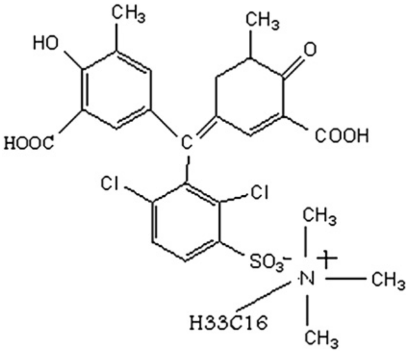

Fig. 1. Chemical structure of CAS–CTAB ion pair.

pink to blue along with an increase of the UO_2^{2+} concentration. The performance of the present test strip for UO_2^{2+} was studied.

2. Experimental

2.1. Reagents

All the chemicals used were obtained from Merck with the highest purity and were used without any further purification. Cetyl *N*,*N*,*N*-trimethyl ammonium bromide (CTAB) and Chromazurol S (C.I. Mordant Blue 29), CAS (trisodium salt of 3″-sulpho-2″,6″-dichloro-3,3′-dimethyl-4-hydroxy fuchson-5,5′-dicarboxylic acid) were purchased from Fluka. Stock solution of uranyl ion was prepared daily by dissolving 0.016 g of uranyl acetate, $UO_2(OAC)_2 \cdot 2H_2O$, in acetate buffer at pH = 4.5 in 25 ml standard flask. Further dilution was made with the acetate buffer at 0.1 mol L^{-1} ionic strength.

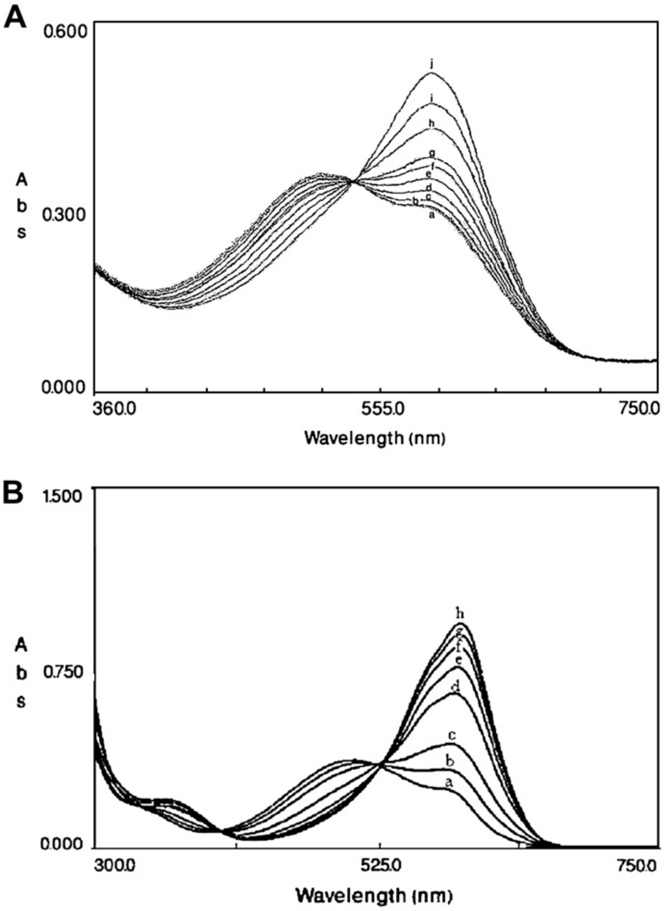

Fig. 2. (A) Absorption spectra of CAS–CTAB in optical test strip in the absence and presence of UO_2^{2+}(a–j: 0, 3.0×10^{-7}, 6.0×10^{-7}, 1.0×10^{-6}, 2.0×10^{-6}, 4.0×10^{-6}, 6.0×10^{-6}, 8.0×10^{-6}, 1.0×10^{-5} and 3.0×10^{-5} mol L^{-1}) in acetate buffer and (B) absorption spectra of CAS in solution after exposure to uranyl ions at the above concentrations.

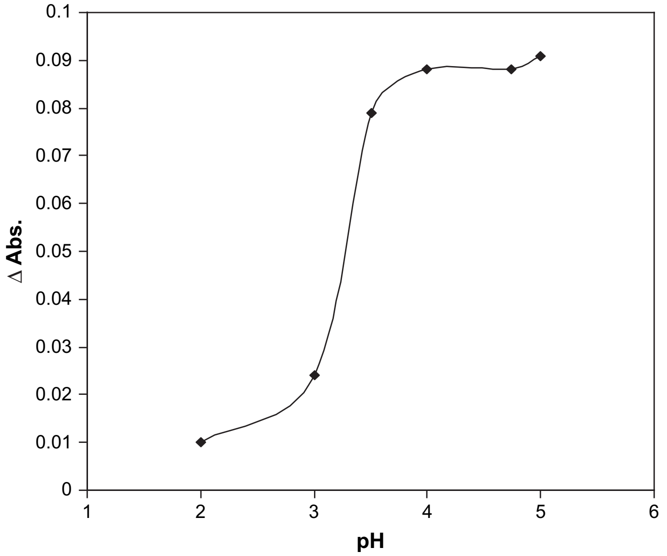

Fig. 3. Effect of uranyl ion solution on the test strip response ($[UO_2^{2+}] = 1.0 \times 10^{-6}$ mol L^{-1}).

2.2. Instrumentation and detection method

The absorbance of the test strips was measured in a 1-cm cuvette using a Shimadzu 2150–PC UV–vis spectrophotometer. The test strip was first exposed to the buffer solution in the cuvette and the absorbance was measured at 598 nm. Then, the sample solution was added and the absorbance was again measured after 15 min at this wavelength. The pH values were determined with a Corning ion analyzer 250-pH/mV meter using a combined glass electrode.

2.3. Preparation of the test strip

The CAS–CTAB ion pair was prepared by dissolving 0.0156 mmol of CAS and CTAB in 20 ml of ethylene diamine. Transparent

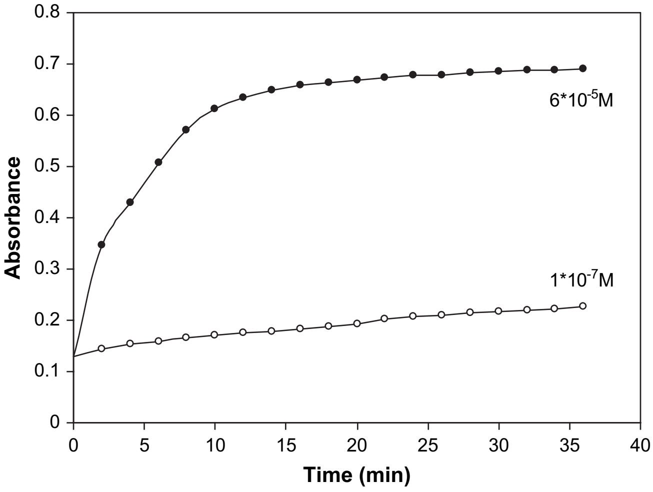

Fig. 4. Response time of the optical test strip at two different concentrations of uranyl ions.

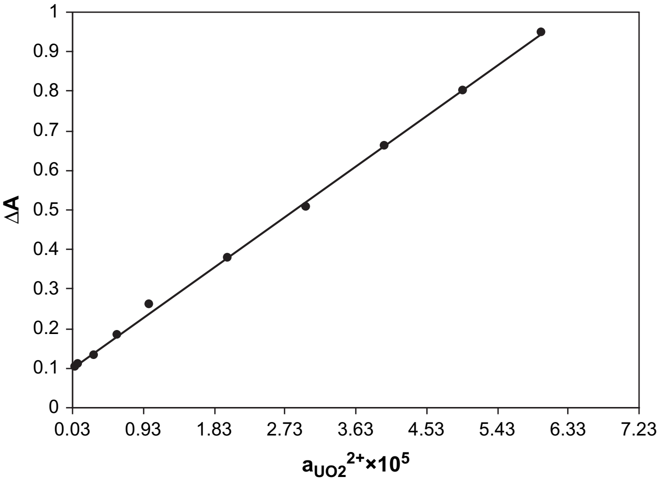

Fig. 5. The optical test strip response versus UO_2^{2+} ion activities at pH = 4.5.

photography film (Konica) tapes which consisted of triacetyl cellulose were used as immobilization matrix and treated with commercial hypochlorite solution to remove the colored gelatinous layers. To convert the acetyl cellulose into cellulose, the membranes were treated with a 50 mmol L^{-1} solution of sodium hydroxide for 5 min and then washed with distilled water. Immobilization of CAS onto the cellulose films was performed by inserting the films into the ion pairing solution for 15 min at the ambient temperature and then washed with distilled water to remove the extra reagent. Then, the films were cut into 9.0 mm × 30.0 mm strips and the strips were kept in the buffer solution for 2 h before measurement.

3. Results and discussion

The response of the optical test strip was optimized taking into consideration the factors related to the design of the selective membrane such as proportion of the components and the conditions used for making the membrane and factors related to the reaction between the analyte and the membrane, such as pH, contact time and uranyl concentration.

3.1. Spectral characteristics

The absorption spectrum of CAS in sensor film showed two absorption maxima located at 510 and 598 nm. In the presence of UO_2^{2+}, an intense band is formed with absorption maximum at 598 nm which could correspond to the formation of the UO_2^{2+}–CAS binary complex .The presence of surfactant favoured the formation of the complex, so the absorbance of the peak at 598 nm increased with increasing concentration of the cationic surfactant, CTAB. Depending on the concentration of the reaction components, ternary compounds were found in solution with UO_2^{2+}–CAS–CTAB ratios equal to 1:1:1 and 1:2:2, i.e., a CAS:CTAB ratio of 1:1. In all these cases, an ionic form of UO_2^{2+}–CAS formed to which the surfactant cation is bound probably through the SO_3^- group. Upon dipping the film into a buffered UO_2^{2+} solution, an increase of the absorption band at 598 nm and a decrease in the absorption band at 510 nm were observed due to the extraction of uranyl ion from the aqueous solution into the membrane (Fig. 2A). The pink colored film successively changed to a blue color along with an increase of the UO_2^{2+} concentration.

Table 1
Analytical figures of merit of the proposed sensor

Parameter	Value
Linear range (mol L^{-1})	3.0×10^{-7}–6.0×10^{-5}
Limit of detection (mol L^{-1})	1.1×10^{-7}
R.S.D%; Intera test strip	±0.55
R.S.D%; inter test strip	±1.64
Working pH	4.5
Cost ($/strip)	0.23

Table 2
Effect of foreign ions on the determination of 1.0×10^{-6} mol L^{-1} of UO_2^{2+}

Foreign ion	Tolerance ratio
Mg^{2+}, Ba^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, K^+, Ca^{2+}, Sr^{2+}, NH_4^+, Cl^-	1000
Ni^{2+}	700
Cd^{2+}, Pb^{2+}, SO_4^{2-}	500
Ag^+	100
La^{3+}	70
$Cr_2O_7^{2-}$	50
Ce^{3+}, MoO_4^{2-}, $C_2O_4^{2-}$, citrate	20
Fe^{3+}	5
Cu^2, Th^{4+}, Zr^{4+}	2

Similar spectra were obtained for the free and the complexed CAS in solution with the maxima located at 467 and 581 nm (Fig. 2B). The red shift in maximum wavelength of the complex in sensing membrane in comparison to that of soluble form, suggested that the immobilized and solution form of the ternary complex exhibit marked difference in the optical properties, due to binding of CAS to the cellulose matrix. Thus, the appearance of the characteristic absorption band at 598 nm is likely to depend on the structure of the complex. It seems the structure of the immobilized dye is more planar than that of its analogue in solution. The wavelength of 598 nm was selected for further studies because of higher selectivity and sensitivity at this wavelength.

3.2. Effect of pH

The effect of pH of a sample on the absorption of the test strip at 598 nm was studied by immersion of the test strip in a solution containing 1.0×10^{-6} mol L^{-1} UO_2^{2+} at the pH range of 2.0–5.0 for 15 min. As can be seen in Fig. 3, the response of the membrane increased by increasing pH of the solution from 2.0 to 4.0 and remained constant in pH range of 4.0–5.0. At higher pH values, the insoluble hydroxyl complexes of uranyl ion resulted.

Responses of the membrane to various buffer solutions such as citrate, phthalate and phosphate (0.1 mol L^{-1}) were also studied and the results showed that it responded best to the acetate buffer. Therefore, the pH of sample solution was subsequently fixed at 4.5 with acetate buffer.

3.3. Response time

The response time of the proposed membrane sensor, defined as the time required to reach 95% of the final signal, was investigated at two different concentrations of uranyl ions, i.e., 6.0×10^{-6} and 1.0×10^{-7} mol L^{-1}. In order to reach an equilibrium state of the absorbance signal, the analyte ion must diffuse through the entire

Table 3
Results of the uranyl determination in ground water samples by the optical test strip

Sample	Added (mol L^{-1})	Found (mol L^{-1}) ($n = 3$)
Station 1	2.00×10^{-6}	$(2.02\pm0.05)\times10^{-6}$
Station 1	6.00×10^{-5}	$(6.30\pm0.06)\times10^{-5}$
Station 2	2.00×10^{-6}	$(1.91\pm0.04)\times10^{-6}$
Station 2	6.00×10^{-5}	$(5.60\pm0.07)\times10^{-5}$

Table 4

Comparison of the analytical parameters of the proposed uranyl-selective test strip with other developed optical sensors

Active material	Linear range ($mol\,L^{-1}$)	Lower limit of detection ($mol\,L^{-1}$)	Interfering ions	Ref.
Arsenazo III	3.7×10^{-8}–3.7×10^{-7}	NM	Ca^{2+}, Th^{4+}	[17]
Alizarin Red S	1.7×10^{-5}–18.7×10^{-5}	5.0×10^{-6}	Cu^{2+}, Th^{4+}, V^{5+}, Al^{3+}	[19]
TOPO–dibenzoylmethane	4.1×10^{-6}–2.0×10^{-4}	2.5×10^{-6}	Pb^{2+}, Tl^{+}, Cs^{+}	[14]
Arsenazo III	1.8×10^{-6}–3.7×10^{-5}	NM	La^{3+}, Th^{4+}, transition metals	[23]
Arsenazo III	1.0×10^{-7}–1.0×10^{-4}	1.0×10^{-7}	Pb^{2+}, Ca^{2+}, Th^{4+}	[24]
Chromazurol S	3.0×10^{-7}–6.0×10^{-5}	1.1×10^{-7}	Cu^{2+}, Fe^{3+}, Zr^{4+}, Th^{4+}	This work

NM = not mentioned.

thickness of the membrane, so it depends on the concentration of UO_2^{2+} ions. The steady state of the absorbance signal was achieved in 15 min for the tested solutions (Fig. 4).

3.4. Analytical parameters

The optical response of the proposed uranyl-selective test strip under optimal experimental conditions is shown in Fig. 5. The activity of the uranyl ions was obtained by calculating activity coefficient (γ) using the extended Debye–Huckel equation. The plot of the difference in absorbance (ΔA) versus UO_2^{2+} ion activity exhibited a linear correlation as $\Delta A = 14{,}125C + 0.0968$ with a correlation coefficient of 0.9995 ($n = 3$) for the range of 3.0×10^{-7}–6.0×10^{-5} $mol\,L^{-1}$ UO_2^{2+} where C is the concentration of uranyl ion in $mol\,L^{-1}$. The limit of detection (LOD) which is defined as the concentration of the sample yielding a signal equal to the blank signal plus three times of its standard deviation was found to be 1.1×10^{-7} $mol\,L^{-1}$ (30 μg L^{-1}).

Measurement repeatability and sensor-to-sensor reproducibility are two important characteristics for the sensor being developed. The repeatability of the test strip in the determination of uranyl ion was evaluated by performing seven determinations with the same standard solution of uranyl ions. The variation coefficient of the sensor response for 1.0×10^{-6} $mol\,L^{-1}$ uranyl solution at pH = 4.5 with the mean absorbance value of 0.277 was ±0.55%. The reproducibility between different membranes ($n = 8$) for 1.0×10^{-6} $mol\,L^{-1}$ uranyl solution was obtained ±1.64%.

It was found that the optical test strip could be stored under wet conditions for 3 days without any measurable change in the absorbance. Table 1 summarized the analytical figures of merit of the developed test strip.

3.5. Regeneration of the test strips

The absorbance signal of the optical test strip was not recovered completely when the solution was switched from high to low uranyl ion concentrations. After immersion of a used test strip for 10 min in a 1.0×10^{-2} $mol\,L^{-1}$ solution of NaF or instantly in a 1.0×10^{-2} $mol\,L^{-1}$ solution of HCl, however, the absorbance was found to be fully recovered. It is confirmed by getting back to the original absorbance signal at an investigated uranyl concentration.

3.6. Interference study

The selectivity of the method was determined by adding different amounts of potentially interfering species to samples containing 1.0×10^{-6} $mol\,L^{-1}$ UO_2^{2+}. The tolerance limit was taken as the concentration of foreign ion causing an error of ±5% in the determination of UO_2^{2+} by means of a test strip. The obtained results are summarized in Table 2. As can be seen from the data, among common cations and anions tested, alkaline, alkaline earth metal and transition metal ions didn't interfere even at high concentrations. Only Cu^{2+}, Fe^{3+} and Th^{4+} showed the serious interferences but in the presence of EDTA, Th^{4+} and Cu^{2+} were masked.

3.7. Determination of UO_2^{2+} in ground water samples

The applicability of the proposed sensor was tested with two different concentrations of UO_2^{2+} ions which were spiked into the ground waters (stations 1 and 2: Bojd and Shokatabad Ganats; Birjand – Iran, respectively) adjusted with acetate buffer at pH 4.5. Before the analysis, the samples were passed through a 0.45 μm membrane filter. The concentration of the uranyl ions was measured using the proposed test strip. The results in Table 3 show good agreement between the added and found amounts of uranyl ions implying that the present test strip can be used for determination of uranyl ion in ground water samples.

3.8. Comparison with other uranyl optical sensors

The performance of the proposed test strip was compared with some of the reported optical sensors (Table 4) [14,17,19,23,24]. The proposed sensor offers the advantages of low detection limit (1.1×10^{-7} $mol\,L^{-1}$), simple construction, low cost and applicability of about two orders of magnitude of concentration without pretreatment steps.

4. Conclusion

The optical sensor described in this work, based on immobilized C.I. Mordant Blue 29–CTAB ion pair on triacetyl cellulose membranes, provides a simple tool for the determination of UO_2^{2+} ions. On reaction with the UO_2^{2+} ions, the sensor showed a change in color from pink to blue. Such a sensor will be extremely user friendly in the sense that it can easily be operated even by a less skilled personnel and does not require excessive calibration.

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References

[1] Gilman AP, Villencuve DC, Secours VE, Yagminas AP, Tracy BL, Quinn JM, et al. Uranyl nitrate: 28-day and 91-day toxicity studies in the sprague-dawley rat. Toxicol Sci 1998;41(1):117–28.

[2] Fujino O, Umetani S, Ueno E, Shigeta K, Matsuda T. Determination of uranium and thorium in apatite minerals by inductively coupled plasma atomic emission spectrometry with solvent extraction separation into diisobutyl ketone. Anal Chim Acta 2000;420(1):65–71.

[3] Joannon S, Telouk P, Pin C. Determination of U and Th at ultra-trace levels by isotope dilution inductively coupled plasma mass spectrometry using a geyser-type ultrasonic nebulizer: application to geological samples. Spectrochim Acta Part B At Spectrosc 1997;52(12):1783–9.

[4] Hirano Y, Ogawa Y, Oguma K. Simultaneous spectrophotometric determination of uranium and thorium by flow injection analysis using selective masking. Anal Sci 2003;19(20):303–7.

[5] Moulin C, Decambox P, Trecani L. Direct and fast uranium determination in zirconium by time-resolved laser-induced fluorescence spectrometry. Anal Chim Acta 1996;321(1):121–6.
[6] Abbaspour A, Baramakeh L. Novel zirconium optical sensor based on immobilization of Alizarin Red S on a triacetylcellulose membrane by using principle component analysis artificial neural network. Sens Actuators B 2005; 114(2):950–6.
[7] Oehme I, Wolfbies OS. Optical sensors for determination of heavy metal ions. Mikrochim Acta 1997;126(3–4):177–92.
[8] Steinberg IM, Lobnik A, Wolfbies OS. Characterisation of an optical sensor membrane based on the metal ion indicator pyrocatechol violet. Sens Actuators B 2003;90(1–3):230–5.
[9] Lerchi M, Bakker E, Rusterholz B, Simon W. Lead-selective bulk optodes based on neutral ionophores with subnanomolar detection limits. Anal Chem 1992; 64(14):1534–7.
[10] Bright FV, Poirier GE, Hieftje GM. A new ion sensor based on fiber optics. Talanta 1988;35(2):113–8.
[11] Mohr GJ, Wolbeis OS. Optical sensors for a wide pH range based on azo dyes immobilized on a novel support. Anal Chim Acta 1994;292(1–2):41–8.
[12] Capitan-Vallvey LF, Fernandez Ramos MD, Alvarez de Cienfuegos Galvez P, Gomez J. Magnesium-selective test strip. Talanta 2005;65(1):239–45.
[13] Oehme I, Prattes S, Wolfbies OS, Mohr GJ. The effect of polymeric supports and methods of immobilization on the performance of an optical copper(II)-sensitive membrane based on the colourimetric reagent Zincon. Talanta 1998; 47(3):595–604.
[14] Shamsipur M, Tashkourian J, Sharghi H. Development of a PVC-membrane ion-selective bulk optode, for UO_2^{2+} ion, based on tri-*n*-octylphosphine oxide and dibenzoylmethane. Anal Bioanal Chem 2005;382(4):1159–62.
[15] Murkovic I, Oehme I, Mohr GJ, Ferber T, Wolfbeis OS. Optode membrane for continuous measurement of silver ions. Mikrochim Acta 1995;121(1–4): 249–58.
[16] Trutneva LM, Shvoeva OP, Savvin SB. Zh Anal Khim 1989;44(10):1804–8.
[17] Savvin SB, Dzherayan TG, Petrova TV, Mikailova AV. Sensitive optical sensors for uranium(VI), mercury(II), and lead. J Anal Chem 1997;52(2):136–40.
[18] Collins GE, Lu Q, Abubeker S, Vajs E. Remote fiber-optic flow cell for the detection of uranium(VI) in groundwater. Appl Spectrosc 2002;56(4):464–8.
[19] Safavi A, Bagheri M. A novel optical sensor for uranium determination. Anal Chim Acta 2005;330(1):55–60.
[20] Oehme I, Prokes B, Murkovic I, Werner T, Klimant I, Wolfbies OS. LED-compatible copper(II)-selective optode membrane based on lipophilized Zincon. Fresenius J Anal Chem 1994;350:563–7.
[21] Strelow F, Van der Walt T. Comparative study of the masking effect of various complexations in the spectrophotometric determination of uranium with arsenazo III and chlorophosphonazo III. Talanta 1979;26(7–9):537–42.
[22] Marczenko Z. Separation and spectrophotometric determination of elements. 1st ed. New York: John Wiley & Sons; 1986. p. 615.
[23] Baylor LC, Buchannan BR. Reflectance probe for uranium(VI) based on the colorimetric indicator Arsenazo III. Appl Spectrosc 1995;49(5):679–81.
[24] Lerchi M, Reitter E, Simon W. Uranyl ion-selective optode based on neutral ionophores. Fresenius J Anal Chem 1994;348(4):272–6.