Research Article

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Fluorescence quenching detection of UO$_2^{2+}$ in aqueous solution based on an organic molecule probe of 6-chloro-2H-1,2,4-benzothiadiazine-7-sulfonamide 1,1-dioxide

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Abstract: A new organic molecule probe has been introduced as a “turn-off” fluorescent sensor to detect trace quantities of UO$_2^{2+}$ in the presence of several transition metals with promising results. The procedure is based on quenching the fluorescence intensity of 6-chloro-2H-1,2,4-benzothiadiazine-7-sulfonamide 1,1-dioxide (L) in the presence of various UO$_2^{2+}$ concentrations in methanol. The UO$_2^{2+}$ and L species interact through electrostatic interaction between negatively charged nitrogen atom of the sulfonamide group of L and positively charged UO$_2^{2+}$, thus facilitating the non-radiative recombination of UO$_2^{2+}$ and L through the charge transfer or electron transfer processes and leading to the fluorescence quenching of L. The mechanism of quenching was addressed and proved to be static quenching. The impressive quenching of the fluorescence intensity of L by different concentrations of UO$_2^{2+}$ has been successfully used as a new sensor to measure UO$_2^{2+}$ in methanol at $\lambda_{ex} = 340$ nm, $\lambda_{em} = 380$ nm with a linear dynamic range of 0.08–5.0 µM and detection limit and quantification limit of 0.0276 and 0.0837 µM, respectively. The L sensor shows interesting advantages compared to other developed sensors with adequate performance, such as broader linear range and lower detection limit, selectivity, and simplicity, which illustrate its useful practical use.

Keywords: fluorescence, UO$_2^{2+}$, quenching, assessment

1 Introduction

The fast development of nuclear industry, such as the extraction of uranium minerals, the generation of nuclear electricity, the treatment of spent fuel, and the manufacturing of nuclear weapons, has produced a residue of uranium pollution in the marine environment, posing a clear threat to the ecological system and to human and animal health [1]. In aqueous solution, uranium has many forms, and the most prevalent one is uranyl (UO$_2^{2+}$) [2–5]. The development of a fast and efficient analytical procedure for UO$_2^{2+}$ recognition enables it to be measured at a very low concentration to avoid its adverse effects on the atmosphere and on the living organism at an early phase. Analytical techniques such as atomic absorption spectrometry [6,7], atomic emission spectrometry [8,9], or mass spectrometry [10,11] are routinely used in conjunction with a sample pretreatment scheme for high sensitivity UO$_2^{2+}$ analysis. However, high cost, advanced and complicated devices, and the needs of skilled staff and well-equipped laboratories limit their use [12–14]. This causes problems for an on-site and real-time detection of heavy metal ions. Developing sensors with sensitivities comparable to those advanced instrumental techniques is a major challenge for a long time to come. This is because several metal ions have the same or almost ion radius, charging or other properties, making it hard to assess.

Fluorescence optical sensor is a very promising tool for potential practical applications due to its precision and its inherent sensitivity [15,16]. But fewer reports of UO$_2^{2+}$ fluorescent sensors have been published. For instance, Chen et al. introduced an aggregation-induced emission-active sensor, 4-pentoxycarboxyl salicylaldehyde azine (PCSA), which displays high sensitivity towards UO$_2^{2+}$ [17]. Also, 2,6-pyridinedicarboxylic acid (PDA) has been used as a fluorescence sensitizing agent for
UO$_2^{2+}$ measurement by Maji and Viswanathan [18]. However, 2,6-pyridinedicarboxylic acid (PDA) interacts with various metal ions which hinder the detection of UO$_2^{2+}$ in the presence of various competing ions. Wu et al. immobilized salophen and fluorescence-labelled oligonucleotide for separation and determination of trace UO$_2^{2+}$ concentration [19]. Ganesh et al. used fluorescence enhancing reagent (sodium pyrophosphate) for the determination of UO$_2^{2+}$ concentration during spent fuel reprocessing [20]. However, by using these sensors, the presence of some transition metals and thorium ions interfered with the UO$_2^{2+}$ detection. In addition, additional chemicals (for instance, oligonucleotide, sodium pyrophosphate, and calcein) or tools are needed to achieve the sensitivity and selectivity. Therefore, in the presence of transitional metals and less chemical uses, the development of highly selective and sensitive fluorescent sensors for UO$_2^{2+}$ recognition remains a challenge.

In the literature, some thiol-based ligands have been found, which have been used for the detection of transition metal ions [21–23]. The present study used thiazide-based ligand as a new organic molecule probe [6-chloro-2H-1,2,4-benzo thiadiazine-7-sulfonamide-1,1-dioxide (L)] for the assessment of UO$_2^{2+}$. The literature review and preliminary study indicated the following: first, L sensor belongs to the thiazide class and has strong fluorescence spectra due to high mobility of its π-electron and high quantum yield. Second, L sensor has high molar absorptivity, which is preferred because the absorption light is increasing at a given wavelength. Third, the preliminary studies of the absorbance and fluorescence emission spectra of L have shown variations that exist when UO$_2^{2+}$ is gradually added to L and the fluorescence emission intensity of L is decreased. Therefore, the concentration of UO$_2^{2+}$ could thus be detected quantitatively. In this regard, L was studied for the application of a new organic molecule probe for spectrofluorometric assessment of UO$_2^{2+}$ in aqueous solution.

2 Experimental

2.1 Materials

The chemicals used in the tests of analytical grade with no further purification. 6-Chloro-2H-1,2,4-benzo thiadiazine-7-sulfonamide-1,1-dioxide (L) was purchased from Sigma-Aldrich. Uranyl nitrate hexahydrate, UO$_2$(NO$_3$)$_2$·6H$_2$O, was manufactured by Mallinckrodt Company. All the other chemicals used in this study were purchased from Alpha Company.

2.2 Instruments

Fluorescence emission spectra were measured using Meslo-PN (Lumina fluorescence Spectrometer; Thermo Scientific, USA). Both emission and excitation slits were at 5.0 nm. The absorption spectra were measured using UV-Vis Evolution 300 (Thermo Fisher Scientific Company, UK). As a reference, UO$_2^{2+}$ was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (iCAP 6500 ICP-OES; Thermo Fisher Scientific, UK). Experiments were carried out in safeguards destructive analysis lab (ETZ-, KMP-I), Nuclear and Radiological Regulatory Authority.

2.3 Analytical procedures

In order to assess the UO$_2^{2+}$ concentration by L sensor, a stock solution of UO$_2^{2+}$ (100 µM) was prepared by dissolving an accurately weighed amount of uranyl nitrate hexahydrate (UO$_2$(NO$_3$)$_2$·6H$_2$O) in deionized water containing few drops of concentrated sulphuric acid and standardized by a known method [24]. All working solutions were prepared by diluting the stock solution suitably with deionized water to give various concentrations of UO$_2^{2+}$ from 0.08 to 5.0 µM. These various concentrations of UO$_2^{2+}$ were added to L (1.0 mL, 100 µM). The solutions have been mixed with 10 mL of methanol. Measurements of the fluorescence emission intensities were carried out at $\lambda_{ex} = 340$ nm, $\lambda_{em} = 380$ nm, and 1 min (to reach the equilibrium). The linear range of the fluorescence emission intensity of L sensor was observed between 0.08 and 5.0 µM of UO$_2^{2+}$ concentrations.

3 Results and discussion

3.1 Preliminary studies

6-Chloro-2H-1,2,4-benzo thiadiazine-7-sulfonamide 1,1-dioxide (L) belongs to the thiazide class. Clearly, it emitted fluorescence as it possessed conjugated functional groups. In addition, its molar absorption is a factor deciding the
selection of L to be studied as a fluorescence sensor. High molar absorption of L is favoured because at a specified wavelength it enhances the absorption of light, so as it interacts with the target analyte, the sensitivity of L enhances. The molar absorptivity of L is $2.0 \times 10^6$ L/mol cm according to Jothieswari et al. [25].

The variations in the absorption and fluorescence emission spectra that appear after the addition of UO$_2^{2+}$ to L (10 µM) have been examined in order to determine that L can be used as a sensitive fluorescent sensor for UO$_2^{2+}$.

The absorbance spectra of L and UO$_2$/L are shown in Figure 1. The L shows three absorption bands, at 230, 270, and 318 nm. This finding was similar to the findings of the literature. When adding UO$_2^{2+}$ to L, the absorption band intensity increased at 230 nm and the absorption band intensity decreased at 318 nm, which is a possible indicator of the formation of UO$_2$/L species.

Fluorescence emission spectra of L in the presence of various concentrations of UO$_2^{2+}$ (8.0 × 10$^{-8}$, 3.0 × 10$^{-7}$, 6.0 × 10$^{-7}$, 9.5 × 10$^{-7}$, 1.5 × 10$^{-6}$, 2.3 × 10$^{-6}$, 2.8 × 10$^{-6}$, 3.5 × 10$^{-6}$, and 5.0 × 10$^{-6}$ M, respectively) are shown in Figure 2. At an excitation wavelength 340 nm, the L sensor shows a characteristic fluorescent emission band at 380 nm.

The experimental results show that with the increase in the UO$_2^{2+}$ concentration, the fluorescence emission intensity decreases and is fully quenched at a UO$_2^{2+}$ concentration of 60.0 µM. This indicates that the fluorescence quenching ability of L sensor is good in the presence of UO$_2^{2+}$. In addition, in the UO$_2^{2+}$ concentration range of 0.08–5.0 µM, the intensity of the fluorescence emission is linearly quenched. The UO$_2^{2+}$ and L species interact through electrostatic interaction between positively charged UO$_2^{2+}$ and negatively charged nitrogen atom of the sulfonamide group of L. It reveals that it is possible to use the chelating reaction between UO$_2^{2+}$ and L to develop a fluorescence sensor for UO$_2^{2+}$ determination. Since the absorbance intensity of L at $\lambda = 318$ nm decreased, and fluorescence emission intensity of L at $\lambda_{ex}/\lambda_{em} = 340/380$ nm decreased as a function of UO$_2^{2+}$ concentration, both indicated the prevalent formation of a UO$_2$/L species.

### 3.2 Mechanism

Scheme 1 shows the mechanism of UO$_2^{2+}$ assessment using L as a fluorescent probe. Initially, when L was free in aqueous solution, they showed strong fluorescence intensity at $\lambda_{ex}/\lambda_{em} = 340/380$ nm. In the presence of UO$_2^{2+}$, the fluorescence of L was quenched significantly. The results indicate that UO$_2^{2+}$ induced fluorescence quenching of L by the chelation of positively charged UO$_2^{2+}$ with negatively charged nitrogen atom of the sulfonamide group of L, thus facilitating the non-radiative recombination of UO$_2^{2+}$ and L through the charge transfer or electron transfer processes and leading to the fluorescence quenching of L. Job’s method of continuous variation was used to study stoichiometry. The plot of absorbance against the UO$_2^{2+}$ mole fraction has shown that the complex formation between UO$_2^{2+}$ and L is with a molar ratio of 1:2. Also, the reaction between UO$_2^{2+}$ and L was studied by spectrofluorometry at
different temperatures (293 and 303 K) (Figure 3) with the Stern–Völmer equation to understand the fluorescence quenching mechanism [26,27]:

\[
\left( \frac{F_0}{F} \right) = 1 + K_{sv}[Q],
\]

where \(F_0\) and \(F\) are the fluorescence emission intensities of \(L\) in the absence and presence of \(UO_2^{2+}\), respectively, \(Q\) is the quencher concentration of \(UO_2^{2+}\), and \(K_{sv}\) is the constant of Stern–Völmer. Stern–Völmer’s plot of \(\frac{F_0}{F}\) versus \([Q]\) at different temperatures (293 and 303 K) is shown in Figure 3. And the calculated \(K_{sv}\) are \(4.8 \times 10^5\) and \(4.6 \times 10^5\) mol\(^{-1}\) at 293 and 303 K, respectively. This result indicates that there is a good agreement between quenching process and the Stern–Völmer equation, which is an indicator for static quenching mechanism because \(K_{sv}\) decreases with increase in temperature.

### 3.3 Inner filter effect (INF)

In fluorescence spectroscopy, the INF is a significant issue that especially affects spectral measurements. \(UO_2^{2+}\) is a fluorescent species and has absorption and fluorescence spectra. The steps that are being carried out in the experimental work to avoid INF are as follows: (1) choose sample with very low concentration to avoid primary INF and (2) select a particular excitation wavelength to reduce the absorption of the sample. The excitation is decreased to 80 nm (\(\lambda_{ex} = 340\)) below the absorption maximum of \(UO_2^{2+}\) (420 nm) to avoid secondary INFs.

### 3.4 Parameter study

#### 3.4.1 Solvent effect

The \(L\) sensor showed the fluorescence emission spectra at \(\lambda_{ex} = 340\) nm in different solvents. The influences of the solvent on the fluorescence emission intensity of \(L\) sensor are shown in Figure 4. The results showed that the fluorescence emission intensity of the \(L\) sensor is much higher in methanol than in other solvents. These could
be due to various influence factors of solvent such as dielectric constant, polarity, etc. The dielectric constant and polarity of methanol ($\varepsilon = 33$, polarity = 0.762), acetonitrile ($\varepsilon = 37.5$, polarity = 0.46), DMF ($\varepsilon = 36.71$, polarity = 0.386), and DMSO ($\varepsilon = 47.24$, polarity = 0.444), respectively, indicate that the fluorescence quantum yield of $L$ is increasing with the decrease in the solvent dielectric constant and with the increase in solvent polarity. In addition, $L$ is more soluble in methanol. Thus, the high fluorescence quantum yields in methanol could be anticipated, and methanol was selected as the best solvent.

### 3.4.2 Concentration effect

In order to determine the influence of the concentration of $L$ sensor, three concentrations of $L$ at 20.0, 10.0, and 6.0 µM were studied. The linear range is 0.05–10.0 µM (RSD 1.04%) at the concentration of 20.0 µM, 0.08–5.0 µM (RSD 1.13%) at the concentration of 10.0 µM, and 0.06–3.0 µM (RSD 1.64%) at the concentration of 6.0 µM. By taking into consideration, in terms of linear range, detection limit, and response time, a good linear relationship is found between fluorescence emission intensity and $L$ concentration. For further examination, the concentration of 10.0 µM for the $L$ sensor was selected.

### 3.4.3 Selectivity study

An important property of the sensor is its selectivity to the analyte compared with other competing metal ions. Interference experiments for the determination of $UO_2^{2+}$ in spiked methanol are conducted prior to the development of the $L$ sensor.

The effects of various potential metal ions (aluminium, barium, calcium, cadmium, cobalt, copper, chromium, iron, lanthanum, magnesium, manganese, nickel, and zinc) likely present in actual samples are investigated by injecting them into solutions containing 5.0 µM of $UO_2^{2+}$ and by handling them as mentioned in the earlier procedure. The tolerance limit is the maximum amount of an ion that causes an error not greater than 5% in the fluorescence emission intensity of the consequent solutions. The findings indicate that the concentrations of aluminium (3.0 mg/L), barium (24.0 mg/L), calcium (22.0 mg/L), cadmium (15.0 mg/L), cobalt (11.0 mg/L), copper (12.0 mg/L), chromium (4.0 mg/L), iron (3.0 mg/L), lanthanum (1.0 mg/L), magnesium (17.0 mg/L), manganese (17.0 mg/L), nickel (13.0 mg/L), and zinc (12.0 mg/L) have little effect on the $L$ sensor fluorescence emission intensity, indicating that the $L$ sensor has sufficient selectivity for $UO_2^{2+}$ assessment.

### 3.5 Analytical figures of merit

The analytical parameters are measured in order to apply the fluorescent $L$ sensor for $UO_2^{2+}$ assessment. As shown in Figure 3, a good linear relation was obtained between $F_0/F$ versus $UO_2^{2+}$ concentration at 293 K. The regression equation was $F_0/F = 1.0326 + 4.8 \times 10^5 [UO_2^{2+}]$ ($R^2 = 0.9992$) within a concentration range of 0.08–5.0 µM. The limit of detection (LOD) is defined as the lowest amount of analyte in a sample, which can be detected but not necessarily quantitated as an exact value. The limit of quantification (LOQ) is defined as the lowest amount of analyte in a sample, which can be quantitatively determined with suitable precision and accuracy. In order to show the sensor constraint, LOD and LOQ were also calculated. According to the ICH guidance, LOD = $3.3S/b$ and LOQ = $10S/b$ (where $S$ is the standard deviation and $b$ is the slope) are tabulated in Table 1. These results suggested that the $L$ sensor could be used as a tool for the assessment of $UO_2^{2+}$ at very low concentration levels.

### 3.6 Application

In order to investigate the validity of the $L$ sensor to various real aqueous samples, the various R&D samples are assessed by the $L$ sensor and compared with the ICP-OES analysis. The various R&D samples spiked with $UO_2^{2+}$ at different concentrations (0.10, 0.30, and 0.50 µM). The

| Parameter | Value |
|-----------|-------|
| $A_{ex}$ (nm) | 340 |
| $A_{em}$ (nm) | 380 |
| Linear range (M) | $8.0 \times 10^{-8}$–$5.0 \times 10^{-6}$ |
| Limit of detection (LOD) (M) | $2.76 \times 10^{-8}$ |
| Limit of quantification (LOQ) (M) | $8.37 \times 10^{-8}$ |
| Standard deviation (SD) | 0.004 |
| Variance (SD²) | $1.6 \times 10^{-5}$ |
| Correlation coefficient ($R^2$) | 0.9992 |
The L sensor was added to the sample and mixed with 10 mL of methanol and then left for 1 min before measurement of the intensity of fluorescence. Table 2 shows the resulting data obtained. It was indicated that the recovery values are in the range of 95.6–105%. Also, the various R&D samples and their spiked samples are measured by ICP-OES analysis.

The results reveal that the UO₂²⁺ concentration detected from the L sensor was in a good agreement with the concentration results using the ICP-OES analysis. To check the accuracy of L sensor, the recovery results and the results from ICP-OES are used. The precision of the L sensor was measured and the three measurements were recorded as relative standard deviation (RSD%) values. The results of RSD% were lesser than 2.5%. These findings indicate that the procedure is precise and can be used for UO₂²⁺ assessment.

Further study is carried out by comparing the analytical parameters of the L sensor with some of other sensors developed, as shown in Table 3 [17,18,28–33]. The table reveals that, with adequate performance, the L sensor has impressive features, including a broader linear range and a lower detection limit, good selectivity, and remarkable simplicity.

Table 2: Application of L chemosensor for assessment of UO₂²⁺ in different samples

| Sample | UO₂²⁺ spiked a | Proposed measured (n = 5) | Reference measured (n = 5) |
|--------|----------------|--------------------------|--------------------------|
|        | UO₂²⁺ average measured a | Recovery% | RSD% c | UO₂²⁺ average measured a | Recovery% | RSD% c |
|        | ± SD b | | | ± SD b | | |
| S1 | 10 | 10.5 ± 0.23 | 105.0 | 2.19 | 10.2 ± 0.09 | 102.0 | 0.88 |
|     | 30 | 31.1 ± 0.34 | 103.7 | 1.09 | 30.5 ± 0.23 | 101.7 | 0.75 |
|     | 50 | 52.4 ± 0.67 | 104.8 | 1.27 | 50.6 ± 0.41 | 101.2 | 0.81 |
| S2 | 10 | 10.4 ± 0.19 | 104.0 | 1.83 | 10.2 ± 0.08 | 102.0 | 0.78 |
|     | 30 | 31.0 ± 0.34 | 103.3 | 1.09 | 30.3 ± 0.22 | 101.0 | 0.73 |
|     | 50 | 51.8 ± 0.49 | 103.6 | 0.95 | 50.8 ± 0.39 | 101.6 | 0.76 |
| S3 | 10 | 10.4 ± 0.18 | 104.0 | 1.73 | 10.2 ± 0.08 | 102.0 | 0.78 |
|     | 30 | 31.2 ± 0.34 | 104.0 | 1.09 | 30.4 ± 0.20 | 101.3 | 0.66 |
|     | 50 | 52.3 ± 0.50 | 104.6 | 0.96 | 50.7 ± 0.38 | 101.4 | 0.75 |
| Tap water | 10 | 9.57 ± 0.12 | 95.7 | 1.24 | 9.87 ± 0.09 | 98.7 | 0.93 |
|     | 30 | 28.7 ± 0.31 | 95.6 | 1.09 | 28.9 ± 0.23 | 96.5 | 0.81 |
|     | 50 | 47.9 ± 0.87 | 95.8 | 1.83 | 48.8 ± 0.38 | 97.6 | 0.78 |
| Seawater | 10 | 10.3 ± 0.13 | 103.4 | 1.26 | 10.2 ± 0.11 | 102.3 | 1.08 |
|     | 30 | 31.4 ± 0.36 | 104.7 | 1.16 | 30.9 ± 0.31 | 103.1 | 1.01 |
|     | 50 | 52.4 ± 0.66 | 104.8 | 1.26 | 51.4 ± 0.48 | 102.8 | 0.93 |

a The values are multiplied by 10⁻⁸ M. b SD, standard deviation, the values are multiplied by 10⁻⁸ M. c %RSD, relative standard deviation.

Table 3: Comparison of the analytical parameters of L chemosensor with some of the developed optical sensors

| Active material | Linear range (M) | Interfering ions | References |
|-----------------|------------------|------------------|------------|
| PCSA | 3.7 x 10⁻⁹–9.2 x 10⁻⁸ | Cu²⁺ | [17] |
| 2,6-Pyridinedicarboxylic acid | 2.6 x 10⁻⁷–8.8 x 10⁻⁶ | Tb³⁺ | [18] |
| Tetraphenylethene (TPE) modified with 2-(4,5-dihydrothiazol-2-yl) phenol | 1.0 x 10⁻⁶–2.0 x 10⁻⁵ | — | [28] |
| Porphyrin-terminated polymeric | 10⁻⁷–10⁻³ | Cu²⁺, Fe³⁺, Ni²⁺, Zn²⁺ | [29] |
| Cyclic peptide | 3.6 x 10⁻⁷–4.2 x 10⁻⁵ | — | [30] |
| Trimetazidine | 4.9 x 10⁻⁸–1.7 x 10⁻⁶ | Th⁴⁺, Al³⁺, Fe³⁺ | [31] |
| Clopidogrel | 1.0 x 10⁻⁹–4.0 x 10⁻⁶ | Th⁴⁺, some transition metals | [32] |
| Furosemide | 7.0 x 10⁻⁷–4.0 x 10⁻⁶ | Al³⁺, Fe³⁺, some transition metals | [33] |
| 6-Chloro-2H-1,2,4-benzothiadiazine-7-sulfonamide-1,1-dioxide | 8.0 x 10⁻⁸–5.0 x 10⁻⁶ | Al³⁺, Fe³⁺, some transition metals | This work |
4 Conclusion

A new turn-off L sensor is studied with regard to the potential application as a fluorescence quenching sensor for UO$_2^{2+}$. In particular, L sensor presents sensitivity and selectivity to UO$_2^{2+}$ (the detection limit is 0.0276 µM), which is among the best reported results. From this, it was believed that the fluorescence L would be providing a promising and practical UO$_2^{2+}$ sensing material.

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References

[1] Xie Y, Chen C, Ren X, Wang X, Wang H, Wang X. Emerging natural and tailored materials for uranium-contaminated water treatment and environmental remediation. Prog Mater Sci. 2019;103:180–234.

[2] Burns PC, Ewing RC. Nuclear fuel in a reactor accident. Science. 2012;335:1184–8.

[3] Nassab HR, Souri A, Javadian A, Amini MK. A novel mercury-free stripping voltammetric sensor for uranium based on electropolymerized N-phenylanthranilic acid film electrode. Sensor Actuat B Chem. 2015;215:360–7.

[4] Geipel G. Some aspects of actinide speciation by laser-induced spectroscopy coord. Chem Rev. 2006;250:844–54.

[5] Rathore DPS. Advances in technologies for the measurement of uranium in diverse matrices. Talanta. 2008;77:9–20.

[6] Yildiz E, Sacmaci S, Kartal S, Sacmaci M. A new chelating reagent and application for coprecipitation in food samples by FAAS. Food Chem. 2016;194:143–8.

[7] Yang S, Jiang S, Hu K, Wen X. Investigation of dispersive solid-phase extraction combined with slurry sampling thermo spray flame atomic absorption spectrometry for the determination of cadmium. Microchem J. 2020;154:104542.

[8] Balaram V. Recent advances in the determination of elemental impurities in pharmaceuticals-status, challenges and moving frontiers. Trend Anal Chem. 2016;80:83–95.

[9] Barin JS, Mello PA, Mesko MF, Duarte FA, Flores EMM. Determination of elemental impurities in pharmaceutical products and related matrices by ICP-based methods: a review. Anal Bioanal Chem. 2016;408:4547–66.

[10] Chandrasekaran K, Karunasagar D, Arunanachalam J. Dispersive liquid–liquid micro extraction of uranium(IV) from groundwater and seawater samples and determination by inductively coupled plasma–optical emission spectrometry and flow injection–inductively coupled plasma mass spectrometry. Anal Methods UK. 2011;3:2140–7.

[11] Moeser C, Kautenburger R, Philipp Beck H. Complexation of europium and uranium by humic acids analyzed by capillary electrophoresis-inductively coupled plasma mass spectrometry. Electrophoresis. 2012;33:1482–7.

[12] Saha A, Deb SB, Sarkar A, Saxena MK, Tomar BS. Simultaneous preconcentration of uranium and thorium in aqueous samples using cloud point extraction. RSC Adv. 2016;6:20109–19.

[13] Zhang H, Cheng X, Chen L, Mo F, Xu L, Fu F. Magnetic beads-based DNA hybridization chain reaction amplification and DNAsyme recognition for colorimetric detection of uranyl ion in seafood. Anal Chim Acta. 2017;956:63–9.

[14] Saha A, Debnath T, Neogy S, Ghosh HN, Saxena MK, Tomar BS. Micellar extraction assisted fluorimetric determination of ultra trace amount of uranium in aqueous samples by novel diglycolamide-capped quantum dot nanosensor. Sensor Actuat B Chem. 2017;253:592–602.

[15] Gui R, Jin H, Bu X, Fu Y, Wang Z, Liu Q. Recent advances in dual-emission ratiometric fluorescence probes for chemo/biosensing and bioimaging of biomarkers. Coord Chem Rev. 2019;383:82–103.

[16] Gui R, Jin H. Recent advances in synthetic methods and applications of photo-luminescent molecularly imprinted polymers. J Photochem Photobiol C. 2019;41:100315.

[17] Chen X, He L, Wang Y, Liu B, Tang Y. Trace analysis of uranyl ion (UO$_2^{2+}$) in aqueous solution by fluorescence turn-on detection via aggregation induced emission enhancement effect. Anal Chim Acta. 2014;847:55.

[18] Maji S, Viswanathan KS. Sensitization of uranium fluorescence using 2,6-pyridinedicarboxylic acid: application for the determination of uranium in the presence of lanthanides. J Lumin. 2009;129:1242.

[19] Wu M, Liao L, Zhao M, Lin Y, Xiao X, Nie C. Separation and determination of trace uranium using a double-receptor sandwich supramolecule method based on immobilized salophen and fluorescence labeled oligonucleotide. Anal Chim Acta. 2012;729:80–4.

[20] Ganesh S, Khan F, Ahmed MK, Velavendan P, Pandey NK, Mudali UK, et al. Determination of ultra traces amount of uranium in raffinates of Purex process by laser fluorimetry. J Radioanal Nucl Chem. 2012;292:331–4.

[21] Nalawade RA, Nalawade AM, Kamble GS, Anuse MA. Rapid. Synergetic extractive spectrophotometric determination of copper(II) by using sensitive chromogenic reagent N“″,N“″-bis[[E-(4-fluorophenyl)]methylidene]thiocarbonohydrazide. Spectrochim Acta A. 2015;146:297–306.

[22] Kamble GS, Kolekar SS, Anuse MA. Synergetic extraction and spectrophotometric determination of copper(II) using...
1-(2,4-dinitro aminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol: Analysis of alloys, pharmaceuticals and biological samples. Spectrochim Acta A. 2011;78:1455–66.

[23] Kamble GS, Kolekar SS, Han SH, Anuse MA. Synergistic liquid-liquid extractive spectrophotometric determination of gold (m) using 1-(2,4-dinitro aminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol. Talanta. 2010;81:1088–95.

[24] Vogel AI. A text book of quantitative inorganic analysis. 3rd ed. London: Longmans; 1975.

[25] Jothieswari D, Anandakumar K, Santhi DV, Vijayakumar B, Priya D, Rathinraj BS. A validated UV spectrophotometric method for the simultaneous estimation of amlodipine besylate, valsartan and hydrochlorothiazide in bulk and in combined tablet dosage rate. J Pharmaceut Biomed Sci. 2010;1–5.

[26] Kadadevarmath JS, Malimath GH, Melavanki RM, Patil NR. Static and dynamic model fluorescence quenching of laser dye by carbon tetrachloride in binary mixtures. Spectrochim Acta A. 2014;117:630–4.

[27] Nilchi A, Dehaghi TS, Garmarodi SR. Kinetics, isotherm and thermodynamics for uranium and thorium ions adsorption from aqueous solutions by crystalline tin oxide nanoparticles. Desalination. 2013;321:67–71.

[28] Wen J, Huang Z, Hu S, Li S, Li W, Wang X. Aggregation-induced emission active tetraphenylethene-based sensor for uranyl ion detection. J Hazard Mater. 2016;318:363.

[29] Shu X, Wang Y, Zhang S, Huang L, Wang S, Hua D. Determination of trace uranyl ion by thermoresponsive porphyrin-terminated polymeric sensor. Talanta. 2015;131:198.

[30] Yang CT, Han J, Gu M, Liu J, Li Y, Huang Z, et al. Fluorescent recognition of uranyl ions by a phosphorylated cyclic peptide. Chem Commun. 2015;51:11769.

[31] Elabd AA, Attia MS. A new thin film optical sensor for assessment of UO$_2^{2+}$ based on the fluorescence quenching of trimetazidine doped in sol gel matrix. J Lumin. 2015;165:179–85.

[32] Elabd AA, Attia MS. Spectrofluorimetric assessment of UO$_2^{2+}$ by the quenching of the fluorescence intensity of Clopidogrel embedded in PMMA matrix. J Lumin. 2016;169:313–8.

[33] Elabd AA, Elhefnawy OA. An efficient and sensitive optical sensor based on furosemide as a new fluoroionophore for determination of uranyl ion. J Fluoresc. 2016;26:271–6.