

# Optimized and validated spectrophotometric method for the determination of uranium(VI) via complexation with meloxicam

Lutfullah\*, Mohd Noor Alam, Nafisur Rahman,  
Syed Najmul Hejaz Azmi

*Department of Chemistry, Aligarh Muslim University, Aligarh 202002, Uttar Pradesh, India*

Received 27 May 2007; received in revised form 15 November 2007; accepted 16 November 2007

Available online 22 November 2007

## Abstract

An optimized and validated spectrophotometric method has been developed for the determination of uranyl ion in the presence of other metal ions. The method is based on the chelation of uranyl ion with meloxicam via  $\beta$ -diketone moiety to produce a yellow colored complex, which absorbs maximally at 398 nm. Beer's law is obeyed in the concentration range of 5–60  $\mu\text{g/mL}$  with apparent molar absorptivity and Sandell's sensitivity of  $5.02 \times 10^4 \text{ L/mol/cm}$  and  $0.1 \mu\text{g/cm}^2/0.001$  absorbance unit, respectively. The method has been successfully applied for the determination of uranyl ion in synthetic mixture and soil samples. Results of analysis were statistically compared with those obtained by Currah's spectrophotometric method showing acceptable recovery and precision.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Spectrophotometry; Uranyl nitrate hexahydrate; Meloxicam; Validation

## 1. Introduction

There has been a renewed interest in low-cost rapid techniques for measuring actinides and other heavy metal elements in environmental water [1,2]. One uranium species of interest is the uranyl ion,  $\text{UO}_2^{2+}$  which is stable, highly soluble and mobile in aqueous phase. Uranyl ion can be found in soils and in low pH-water run off in and around nuclear waste sites and processing facilities. The uranyl unit consists of a uranium centre with a formal charge of +6 coordinated to two double bonded oxygen atoms for a linear dioxo cation. This unit is highly stable and binds to other ligands via the formation of U–O bonds in a plane perpendicular to the axis of the uranyl ion.

There are various techniques such as thin layer chromatography [3], gravimetry [4], titrimetry [5], fluorimetry [6,7], potentiometry [8], polarography [9], X-ray fluorescence [10], inductively coupled plasma mass spectrometry [11] and spectrophotometry [12–18] for the determination of uranium. The

method based on gravimetry requires absence of or prior separation of interfering elements. Volumetric method involves multiple steps and the use of many reagents. Fluorimetry being a sensitive technique is applicable to low levels of uranium. Electroanalytical techniques in general are not preferred on a routine basis. X-ray fluorescence, a wavelength dispersive method is not sensitive enough for the estimation at low levels and is cost effective. Spectrophotometry is increasingly employed in process control owing to its simplicity and adaptability. Most of the reported spectrophotometric methods are tedious and time consuming because they involve prior separation of uranium from impurities by solvent extraction and reduction of Fe(III) to Fe(II) to avoid interference followed by the addition of chromophoric reagents such as thiocyanate [19], hydrogen peroxide [20], hexacyanoferrate(II) [21] and malachite green [22] to the organic phase. Therefore, there is need for a simple and selective spectrophotometric method for the determination of uranium in the presence of some other metal ions. The proposed method is based on the reaction of uranyl ion with meloxicam in 1,4-dioxan-water medium to form a yellow colored complex which absorbs maximally at 398 nm.

\* Corresponding author. Tel.: +91 571 2703515.

E-mail address: [lutfullah786@gmail.com](mailto:lutfullah786@gmail.com) (Lutfullah).

## 2. Experimental

### 2.1. Materials

A Spectronic 20D<sup>+</sup> spectrophotometer (Milton Roy, U.S.A.) with matched glass cells was used for all spectral and absorbance measurements. An Elico model Li-10 pH meter was used to measure pH of the solutions.

### 2.2. Standard solutions

All chemicals used were of analytical or pharmaceutical grade.

- 0.05% uranyl nitrate hexahydrate (CAS: 13520-83-7, Fluka Chemie AG, Darmstadt, Germany) was prepared in distilled water.
- 0.05% meloxicam (CAS: 71125-38-7, Merck, USA) was prepared in 1,4-dioxan.

### 2.3. Recommended procedure for the determination of uranyl ion

Aliquots of 0.1–1.2 mL of standard uranyl nitrate hexahydrate solution (0.05%) were pipetted into a series of 10 mL standard volumetric flasks. Then 1.8 mL of 0.05% meloxicam solution was added in each flask and diluted to 10 mL with distilled water. The contents of each flask was mixed well at room temperature ( $25 \pm 1$  °C) and the absorbance was measured at 398 nm against the reagent blank prepared similarly within the stability time period of 1 d. The concentration of uranyl ion was calculated either from a calibration curve or regression equation.

### 2.4. Study of interferences of metal ions

To study the interferences of metal ions on the determination of uranyl ion, varying amounts of different metal ions such as Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup> and Zn<sup>2+</sup> were mixed with 450 µg of uranyl ion in 10 mL standard volumetric flask and determined by the proposed procedure.

### 2.5. Determination of uranyl ion in soil

Each digested soil sample of our locality was analyzed for uranium but tested negative. Therefore, air-dried soil samples (500 mg) with 50 mg of uranyl nitrate hexahydrate were placed in a closed platinum crucible. The sample was digested with 2 mL of H<sub>2</sub>SO<sub>4</sub> following the method recommended by Hughes and Carswell [23]. The content of the crucible was cooled and transferred it to ice-cold water. The mixture was stirred until all the soluble matters had dissolved and then filtered through Whatmann no. 42 filter paper (Whatmann International Limited, Kent, UK) in 100 mL standard volumetric flask and was diluted up to the mark with distilled water. 20 mL of this solution was percolated through the column packed with Amberlite IR 400.

The column was washed with 0.1 M H<sub>2</sub>SO<sub>4</sub> to remove unadsorbed species. The uranyl ion was eluted with 2 M H<sub>2</sub>SO<sub>4</sub> at a flow rate of 2 mL per minute. After evaporation 10 mL of distilled water was added. The pH of the solution was adjusted to 4 by the addition of ammonia and the final volume of the solution was maintained to 20 mL. The concentration of uranyl ion was determined by the proposed procedure and the reference method [19].

### 2.6. Procedure for reference method [19]

Into a series of 25 mL standard volumetric flasks, different volumes (0.125–1.5 mL) of 0.1% uranyl nitrate hexahydrate were pipetted. To each flask, 10 mL of 0.2 N HCl, 2.0 mL of 10% SnCl<sub>2</sub>·2H<sub>2</sub>O in 1.16 N HCl, 7 mL of 6.57 M NH<sub>4</sub>SCN and diluting to volume with distilled water. The absorbance was measured at 365 nm against the reagent blank prepared similarly except uranyl nitrate hexahydrate. The amount of the uranyl ion in a given sample was computed from the calibration graph or linear regression equation.

### 2.7. Determination of stoichiometry

The stoichiometry of the reaction was studied by Job's method of continuous variations. For this, different volumes (0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0 mL) of  $1.42 \times 10^{-3}$  M uranyl nitrate hexahydrate was added with different volumes (2, 1.8, 1.6, 1.4, 1.2, 1.0, 0.8, 0.6, 0.4, 0.2, 0 mL) of  $1.42 \times 10^{-3}$  M meloxicam and diluted to volume with distilled water in 10 mL standard volumetric flask. The absorbance was recorded at 398 nm and was plotted against the mole fraction of uranyl nitrate hexahydrate.

### 2.8. Validation

The proposed method has been validated for accuracy and precision, linearity, selectivity, recovery, limits of detection and quantitation.

#### 2.8.1. Accuracy and precision

The accuracy and precision of the proposed method was evaluated by replicate analysis ( $n=5$ ) of calibration standards at three concentration levels, i.e. 15, 30 and 60 µg/mL. Five sample solutions of each concentration were analyzed within one day (intra day precision) and in five consecutive days (inter day precision).

#### 2.8.2. Linearity

The linearity of the proposed method was investigated by replicate analysis ( $n=5$ ) at nine concentration levels, i.e. 5, 10, 15, 25, 30, 40, 45, 50, and 60 µg/mL. The absorbance obtained at each concentration was plotted against the initial concentration of uranyl nitrate hexahydrate and the linear regression equation was evaluated by statistical treatment of calibration data. The other regression characteristics were calculated using Origin Software.

The limits of detection and quantitation were calculated using the relations:

$$\text{LOD} = 3.3 \times \frac{S_0}{b} \quad (1)$$

and

$$\text{LOQ} = 10 \times \frac{S_0}{b} \quad (2)$$

where  $S_0$  is the standard deviation of the calibration line and  $b$  is the slope.

### 2.8.3. Selectivity

The selectivity of the proposed method was evaluated by determining the concentration of uranyl ion in the presence of various metal ions such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$ .

### 2.8.4. Recovery experiments

The recovery of uranyl ion from synthetic mixture sample was estimated by the standard addition method. For this purpose, 4 mL (or 8 mL) of sample solution was spiked with 1, 2, 3 and 4 mL of reference standard solution ( $0.5 \mu\text{g/mL}$ ) in a 100 mL standard volumetric flask and the mixture was diluted up to the mark with distilled water. Each level was repeated five times. The nominal value was determined by the proposed procedure.

### 2.8.5. Robustness

The robustness of the proposed method relative to each operational parameter was judged by analyzing the content of uranyl ion in synthetic mixture sample. A synthetic mixture sample solution containing  $50 \mu\text{g/mL}$  of uranyl nitrate hexahydrate was assayed five times using the proposed method. Mean percentage recovery and relative standard deviation were calculated by standard methods.

### 2.8.6. Evaluation of bias

The point and interval hypothesis tests have been performed to compare the results of the proposed method with those of the reference method at 95% confidence level. The bias was evaluated by an interval hypothesis test based on the mean values of the proposed method (method 1) and the reference method (method 2). The test method is considered acceptable when its true mean is within  $\pm 2.0\%$  of that of the reference method using the following quadratic equation [24]:

$$\theta^2 \left( \frac{\bar{x}_1^2 - S_p^2 t_{\text{tab}}^2}{n_1} \right) + \theta(-2\bar{x}_1\bar{x}_2) + \left( \frac{\bar{x}_2^2 - S_p^2 t_{\text{tab}}^2}{n_2} \right) = 0$$

## 3. Results and discussion

A yellow colored complex with maximum absorption at 398 nm was obtained (Fig. 1) when uranyl ion was allowed to react with meloxicam in 1,4-dioxan-water medium while the meloxicam in 1,4-dioxan-water medium did not show any absorbance at 398 nm. The reaction was carried out at  $25 \pm 1^\circ\text{C}$

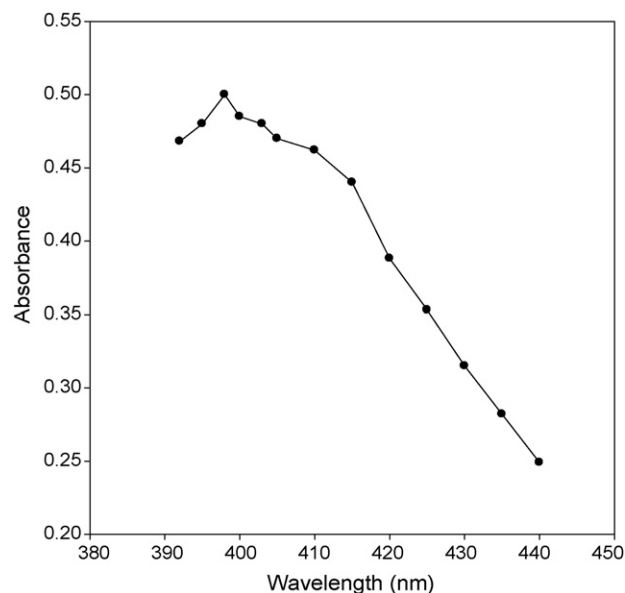


Fig. 1. Absorption spectrum of colored complex:  $500 \mu\text{g}$  uranyl nitrate hexahydrate +  $1.8 \text{ mL}$  of  $1.42 \times 10^{-3} \text{ M}$  meloxicam in 1,4-dioxan. The mixture was diluted to  $10 \text{ mL}$  with distilled water.

and the absorbance of the colored complex was measured immediately at 398 nm. Therefore, the absorbance measurement as a function of initial concentration of uranyl ion was utilized to develop a rapid and selective spectrophotometric method for the determination of uranium(VI).

### 3.1. Stoichiometry

The stoichiometry was established by Job's method of continuous variation. This is due to the interaction of uranyl ion with meloxicam at 398 nm. The plot of absorbance versus mole fraction of uranyl ion has confirmed that 1 mol of uranyl ion reacted

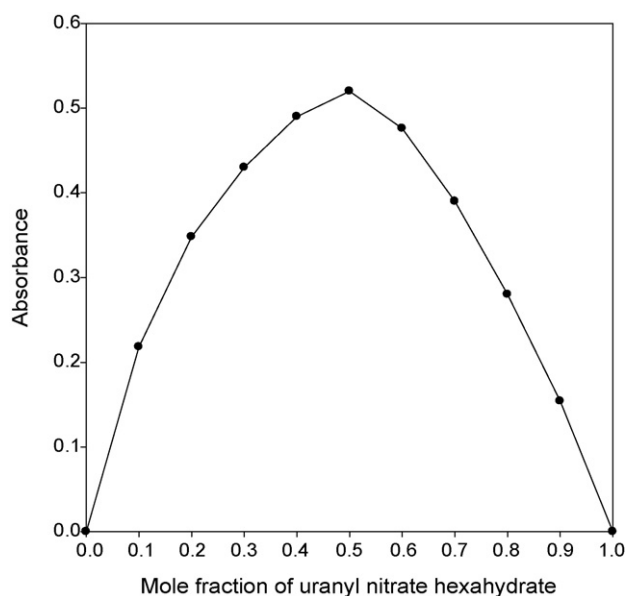
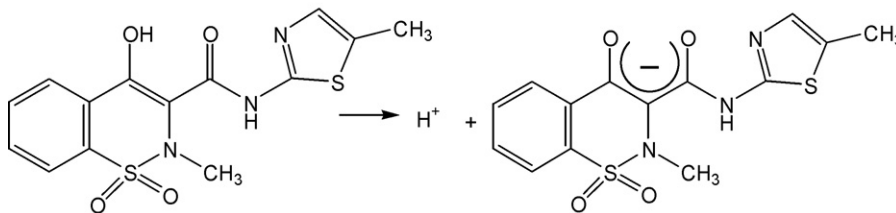


Fig. 2. Job's method of continuous variations of uranyl nitrate hexahydrate-meloxicam complex.

**Step 1****Step 2**

Meloxicam

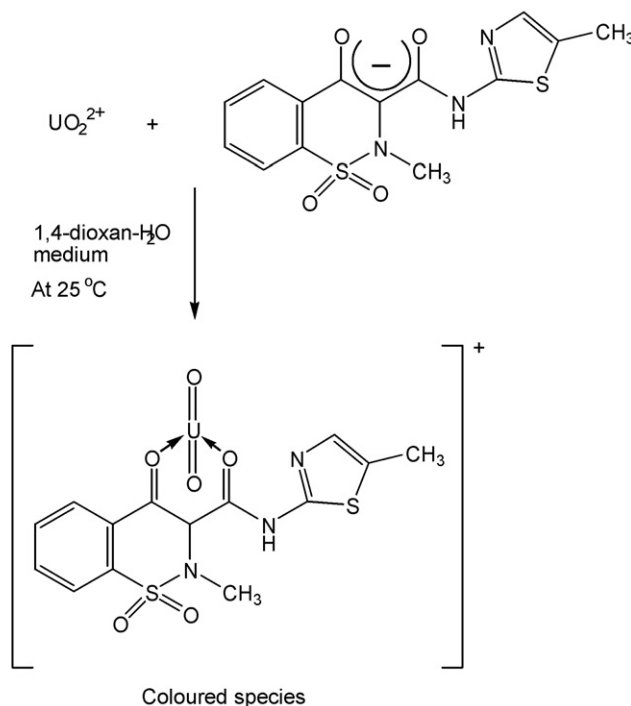
**Step 3**

Fig. 3. Reaction mechanism.

with 1 mol of meloxicam (Fig. 2). The resulting colored complex remained stable for about 24 h. Therefore, it is apparent from the figure that the combining molar ratio between uranyl ion and meloxicam is 1:1. The apparent formation constant and standard Gibbs free energy ( $\Delta G^\circ$ ) were calculated and found to be  $3.91 \times 10^5$  and  $-31.91$  kJ/mol, respectively.

**3.2. Mechanism**

The affinity of piroxicam for metal ions was investigated and found that piroxicam chelates with some cations to form metal ligand complexes [25,26]. In the similar manner meloxicam chelates with uranyl ion via  $\beta$ -diketone moiety to form a

Table 1  
Test of accuracy and precision of the proposed method

Parameters	Intra day assay			Inter day assay		
	15	30	60	15	30	60
Concentration taken ( $\mu\text{g}/\text{mL}$ )	15	30	60	15	30	60
Concentration found ( $\mu\text{g}/\text{mL}$ )	15.016	30.246	60.267	15.096	30.066	59.946
Standard deviation <sup>a</sup> ( $\mu\text{g}/\text{mL}$ )	0.158	0.235	0.195	0.239	0.268	0.271
Recovery (%)	100.11	100.82	100.44	100.64	99.91	100.22
Relative standard deviation (%)	1.06	0.78	0.32	1.59	0.898	0.46
Standard analytical error (%)	0.071	0.105	0.087	0.107	0.120	0.121
Confidence limit <sup>b</sup>	0.200	0.292	0.243	0.300	0.333	0.336

<sup>a</sup> Mean for five independent determinations.

<sup>b</sup> Confidence limit at 95% confidence level and four degrees of freedom ( $t=2.776$ ).

yellow colored complex which absorbs maximally at 398 nm. Therefore, based on the literature background [25,26] and our experimental findings, the reaction mechanism was proposed and is given in Fig. 3.

### 3.3. Optimization

The concentration of meloxicam used for method development was optimized by performing a series of experiments. The influence of the volume of  $1.42 \times 10^{-3}$  M meloxicam on the absorbance of the color developed at constant uranyl nitrate hexahydrate concentration ( $45.0 \mu\text{g/mL}$ ) was examined in the range 0.1–2.2 mL of  $1.42 \times 10^{-3}$  M meloxicam. It is clear from Fig. 4 that the maximum absorbance was attained with 1.4 mL of  $1.42 \times 10^{-3}$  M meloxicam; above this volume upto 2.2 mL, the absorbance remained unchanged. Therefore, 1.8 mL of  $1.42 \times 10^{-3}$  M meloxicam was used in all further measurements.

### 3.4. Validation

#### 3.4.1. Accuracy and precision

The accuracy and precision of the proposed method was evaluated at three concentration levels: 15, 30 and  $60 \mu\text{g/mL}$ . The results of the analysis are summarized in Table 1. It is evident from the table that %recovery and relative standard deviation were in the range of 99.91–100.82% and 0.32–1.59% for the proposed method. These results indicated that there is a satisfactory recovery with low values of %R.S.D.

#### 3.4.2. Linearity

The calibration curve was constructed by plotting absorbance against initial concentration of uranyl ion for the proposed method. Beer's law was obeyed in the concentration range of 5–60  $\mu\text{g/mL}$  with apparent molar absorptivity and sandell's sensitivity of  $5.02 \times 10^4 \text{ L/mol/cm}$  and  $0.1 \mu\text{g/cm}^2/0.001$  absorbance unit, respectively. The calibration data was fitted to the equation,  $A = a + bC$ , where  $A$  is the absorbance at relevant  $\lambda_{\text{max}}$ ;  $C$  is the concentration in  $\mu\text{g/mL}$ ;  $b$  is the slope and  $a$  is the intercept of calibration. The regression parameters are

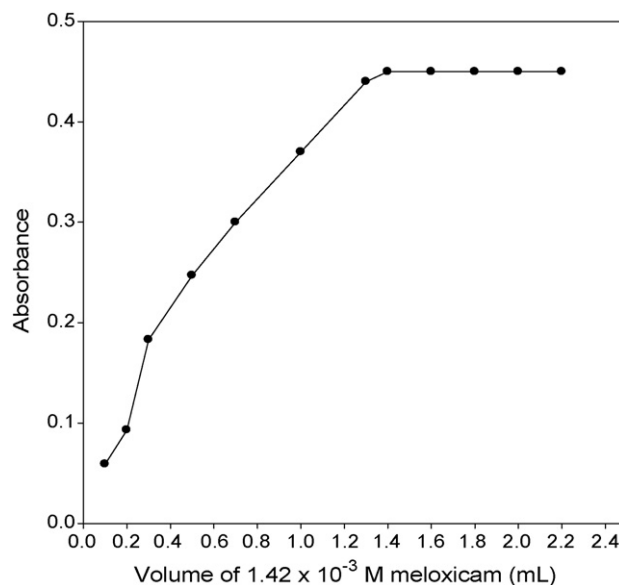


Fig. 4. Effect of the volume of  $1.42 \times 10^{-3}$  M meloxicam.

summarized in Table 2. The high value of correlation coefficient (0.9999) for the proposed method indicated excellent linearity. In order to verify that the proposed methods are free from procedural error, the experimental intercept of the calibration line was tested for significance of the deviation from the theoretical intercept i.e. zero. For this justification, the value of  $t$ -calculated from the relation,  $t = a/S_a$  [27] was found to be 1.524, which did not exceed the theoretical  $t$ -value (2.365) at 95% confidence level. This indicated that the intercept for the proposed method is not significantly different from zero.

The error ( $S_c$ ) [28] in the determination of a given concentration of uranyl ion ( $C$ ) was calculated using statistical analysis of the calibration data and was shown graphically (Fig. 5) by plotting  $S_c$  versus concentration of uranyl ion ( $\mu\text{g/mL}$ ). It is evident from the graph that the error is reached minimum at about  $31.10 \mu\text{g/mL}$  of uranyl ion, thus confirming the level of precision in the range of concentrations examined. The value of  $S_c$  also allowed establishing the confidence limit at the selected value of significance for the determination of unknown concen-

Table 2  
Regression characteristics of analytical data of the proposed and reference methods

Parameters	Proposed method	Reference method
Wavelength (nm)	398	365
Beer's law limit ( $\mu\text{g/mL}$ )	5.0–60	5.0–60
Molar absorptivity ( $\text{L/mol/cm}$ )	$5.02 \times 10^4$	$6.25 \times 10^3$
Sandell's sensitivity	$0.1 \mu\text{g/cm}^2/0.001$ absorbance unit	–
Linear regression equation	$A = 1.140 \times 10^{-3} + 9.98 \times 10^{-3} C$	$A = 7.153 \times 10^{-4} + 7.48 \times 10^{-3} C$
$\pm tS_a$	$1.770 \times 10^{-3}$	$4.600 \times 10^{-3}$
$\pm tS_b$	$4.929 \times 10^{-5}$	$1.277 \times 10^{-4}$
Correlation coefficient ( $r$ )	0.99998	0.99989
Variance ( $S_0^2$ ) of calibration line	$1.254 \times 10^{-6}$	$6.200 \times 10^{-6}$
Detection limit ( $\mu\text{g/mL}$ )	0.370	1.099
Quantitation limit ( $\mu\text{g/mL}$ )	1.122	3.329

$\pm tS_a$  and  $\pm tS_b$  are confidence limits for intercept and slope, respectively.

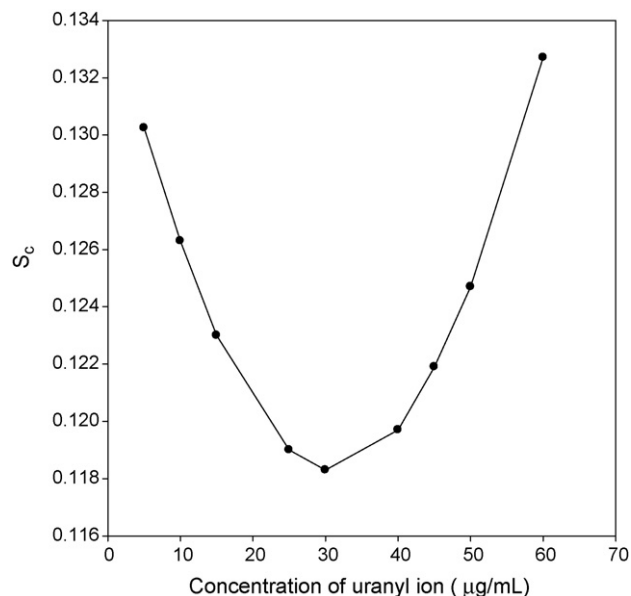
Fig. 5. Error ( $S_c$ ) in the determination of uranyl ion.

Table 3  
Tolerance limit for different type of metal ions

Metal ions	Added as	Tolerance limit (mg) per 45 µg/mL
Na <sup>+</sup>	NaCl	0.125
Mg <sup>2+</sup>	MgCl <sub>2</sub> ·6H <sub>2</sub> O	0.100
Ca <sup>2+</sup>	Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	0.125
Ni <sup>2+</sup>	NiCl <sub>2</sub> ·6H <sub>2</sub> O	0.100
Mn <sup>2+</sup>	MnCl <sub>2</sub> ·4H <sub>2</sub> O	0.015
Zn <sup>2+</sup>	ZnSO <sub>4</sub> ·5H <sub>2</sub> O	0.015

trations by using the relation,  $C_i \pm tS_c$ . The results are shown in Fig. 6 by plotting uncertainty (%  $\Delta C/C$ ) versus the concentration of uranyl ion (µg/mL) at 95% confidence level for  $n-2$  degrees of freedom. Thus, the confidence limit can be established and the relative uncertainty can be achieved directly on the concentration over the full range of the concentration tested.

### 3.4.3. Selectivity

Table 3 shows that the method is selective for the determination of uranyl ion in the presence of specified metal ions.

Table 4  
Recovery results of uranyl ion

Concentration (µg/mL)		Proposed method		Reference method		Paired $t$ - and $F$ -values <sup>b</sup>	$\theta_L^c$	$\theta_U^c$
Sample taken	Standard added	Amount found (µg/mL)	Recovery <sup>a</sup> (%)	Found (µg/mL)	Recovery <sup>a</sup> (%)			
20.0	0, 5, 10, 15, 20	19.93	99.64	–	–	–	–	–
40.0	0, 5, 10, 15, 20	40.12	100.30	–	–	–	–	–
60.0 <sup>d</sup>	–	59.95	99.91	60.04	100.06	$t=0.239$ $F=1.555$	0.981	1.016

<sup>a</sup> Mean for five independent analyses.

<sup>b</sup> Theoretical  $t$ - ( $\nu=8$ ) and  $F$ -values ( $\nu=4, 4$ ) at 95% confidence level are 2.306 and 6.39, respectively.

<sup>c</sup> A bias, based on recovery experiments, of  $\pm 2\%$  is acceptable.

<sup>d</sup> Synthetic mixture contains: 60 µg/mL of uranyl ion with Na<sup>+</sup> (0.0125 mg/mL), Mg<sup>2+</sup> (0.01 mg/mL), Ca<sup>2+</sup> (0.0125 mg/mL), Ni<sup>2+</sup> (0.01 mg/mL), Mn<sup>2+</sup> (0.0015 mg/mL) and Zn<sup>2+</sup> (0.0015 mg/mL).

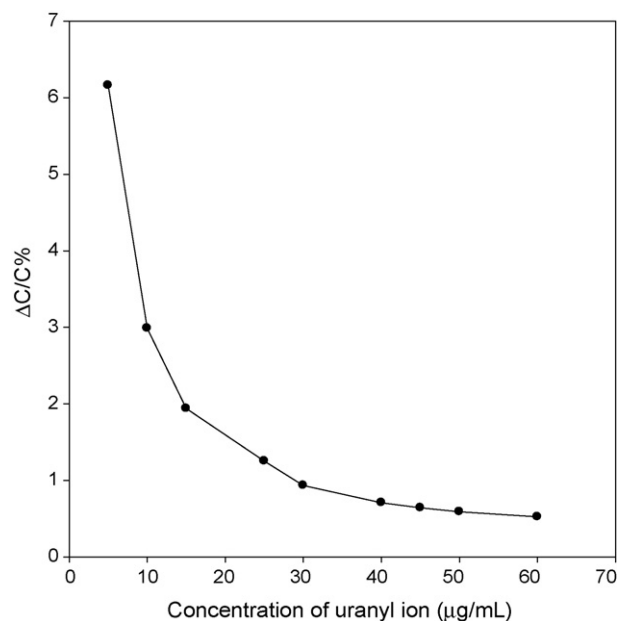


Fig. 6. Plot of percentage uncertainty versus the concentration of uranyl ion at 95% confidence limit.

Table 5  
Determination of uranyl ion in soil samples

Sample	Proposed method		Reference method	
	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
Soil 1	99.10	1.10	98.95	1.35
Soil 2	98.20	1.40	98.60	1.50
Soil 3	98.65	1.22	99.15	1.15

However, the method was found to be less selective in the presence of Cd<sup>2+</sup>, Zr<sup>4+</sup>, Fe<sup>2+</sup>, Al<sup>3+</sup> and Cu<sup>2+</sup>.

### 3.4.4. Recovery

The accuracy of the proposed method was also tested by performing recovery experiments through the standard addition method. The recovery was evaluated either by dividing the intercept by the slope value of the line of linear regression of the standard addition method or by the extrapolation of the same line of best fit (Fig. 7, Table 4). It is evident from Table 4 that the linearity of the regression line of the standard addition method

Table 6  
Comparison of the proposed method with existing UV–vis spectrophotometric methods for the determination of uranyl ion

Reagents	$\lambda_{\max}$ (nm)	Beer's law limit ( $\mu\text{g/mL}$ )	Molar absorptivity (L/mol/cm)	Analysis time (min)	Refs.
8-Quinolinol	380	2–40	$1.50 \times 10^4$	10	[12] <sup>a</sup>
4-(2-Pyridylazo)resorcinol	530	0–7	$3.87 \times 10^4$	15	[13]
Chromazurol S	625	0–2	$9.9 \times 10^4$	15	[14]
Anthranilic acid and rhodamine 6G	575	0.04–4	$6.25 \times 10^4$	15	[15]
<i>p</i> -Carboxychlorophosphonazo	714	4–12	$1.78 \times 10^5$	Immediately	[17]
$\text{SnCl}_2 \cdot \text{H}_2\text{O}$ and $\text{NH}_4\text{SCN}$	365	5–60	$6.25 \times 10^3$	Immediately	[19] <sup>b</sup>
Meloxicam	398	5–60	$5.02 \times 10^4$	Immediately at $25 \pm 1^\circ\text{C}$	This work

<sup>a</sup> Extractive method.

<sup>b</sup> Reference method.

was good. The attractive feature of the method is its relative freedom from other metal ions present in the synthetic mixture sample.

### 3.4.5. Robustness

The robustness of the proposed method relative to the concentration of meloxicam was closely monitored. The concentration of meloxicam examined was as follows:

- $1.42 \times 10^{-3}$  M meloxicam, 1.8 mL ( $\pm 0.4$  mL).

The robustness of the proposed method was judged by analyzing uranyl ion contents in synthetic mixture sample under deliberate small changes in experimental conditions. The results showed that the mean %recovery  $\pm$  R.S.D. was found to be  $99.91 \pm 0.15$  for the proposed method.

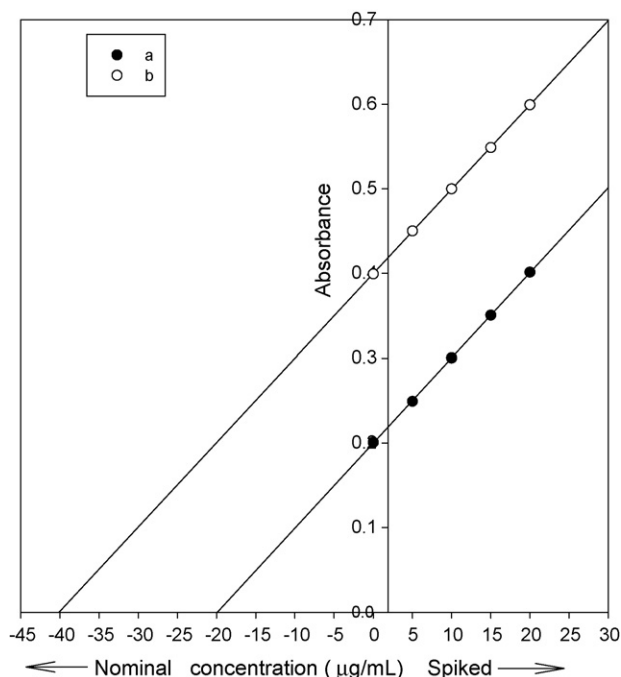


Fig. 7. Plot for the recovery evaluation of uranyl ion through standard addition method: (a) 20 and (b) 40  $\mu\text{g/mL}$ .

### 3.4.6. Evaluation of bias

The proposed method has been successfully applied to the determination of uranyl ion in synthetic mixture sample. The results obtained by the proposed method were compared to those of the Currah's spectrophotometric method [19] using point and interval hypothesis tests. The results (Table 4) show that the Student's *t*- and *F*-values at 95% confidence level are less than the theoretical values, which confirmed that there is no significant difference between the performance of the proposed method and the reference method. The interval hypothesis test has also confirmed that no significant difference exists between the performances of the methods compared, as the true bias of all synthetic mixture sample is  $< \pm 2.0\%$ .

The performance of the proposed procedure is also judged by the analysis of soils taken from different locations. The results are compared with those obtained by the reference method. Table 5 shows that the results were in good agreement with the reference method [19].

The performance of the proposed method was compared with that of other existing UV–vis spectrophotometric methods (Table 6). It is clear from the table that the proposed method is simple and requires less time to complete the analysis. The proposed method has the advantage of using one reagent i.e. meloxicam and comparable sensitivity. The method is versatile, accurate and useful due to high tolerance limits from cations and anions.

## References

- [1] A.F. Arruda, A.D. Campiglia, B.P.S. Chauhan, P. Boudjouk, New organosilicon polymer for the extraction and luminescence analysis of uranyl in environmental samples, *Anal. Chim. Acta* 396 (1999) 263–272.
- [2] C. Moulin, P. Decambox, P. Mauchain, D. Pouyat, L. Coustou, Direct uranium(VI) and nitrate determinations in nuclear reprocessing by time-resolved laser-induced fluorescence, *Anal. Chem.* 68 (1996) 3204–3209.
- [3] T. Hodisan, M. Curtui, S. Cobzac, C. Cimpoiu, I. Haiduc, The limit of detection improvement in TLC determination of uranium and thorium in the presence of other metal ions, *J. Radioanal. Nucl. Chem.* 238 (1998) 179–182.
- [4] P.L. Lopez-de-Alba, S. Gonzalez, J. Gomez Lara, Gravimetric determination of uranyl ion with 2-hydroxy-1-naphthaldehyde/2H-1N/, *J. Radioanal. Nucl. Chem.* 136 (1989) 203–210.
- [5] A.S. Al Ammar, H.M. Basheer, Further development in the high-precision volumetric method for the determination of uranium in nuclear-grade uranium compounds, *J. Radioanal. Nucl. Chem.* 171 (1993) 435–441.

- [6] K.B. Hong, K.W. Jung, K.H. Jung, Application of laser-induced fluorescence for determination of trace uranium, europium and samarium, *Talanta* 36 (1989) 1095–1099.
- [7] D.A. Nivens, Y. Zhang, S.M. Angel, Detection of uranyl ion via fluorescence quenching and photochemical oxidation of calcein, *J. Photochem. Photobiol. A: Chem.* 152 (2002) 167–173.
- [8] M. Anwar, D. Mohammad, Potentiometric determination of free acidity and uranium in uranyl nitrate solutions, *J. Radioanal. Nucl. Chem.* 134 (1989) 45–51.
- [9] M. Mlakar, M. Branica, Stripping voltammetric determination of trace levels of uranium by synergic adsorption, *Anal. Chim. Acta* 221 (1989) 279–287.
- [10] A.W. McMahon, Application of analytical methods based on X-ray spectroscopy to the determination of radionuclides, *Sci. Total Environ.* 130 (1993) 285–295.
- [11] F.A. Aydin, M. Soylak, Solid phase extraction and preconcentration of uranium(VI) and thorium(IV) on Duolite XAD761 prior to their inductively coupled plasma mass spectrometric determination, *Talanta* 72 (2007) 192–197.
- [12] K. Motojima, H. Yoshida, K. Izawa, Spectrophotometric determination of small amounts of uranium with 8-quinolinol, *Anal. Chem.* 32 (1960) 1083–1085.
- [13] T.M. Florence, Y. Farrar, Spectrophotometric determination of uranium with 4-(2-pyridylazo) resorcinol, *Anal. Chem.* 35 (1963) 1613–1616.
- [14] C.L. Leong, T.M. Florence, Y. Farrar, Spectrophotometric determination of uranium(VI) with chromazurol S and cetylpyridinium bromide, *Anal. Chem.* 45 (1973) 201–203.
- [15] T.V. Ramakrishna, R.S.S. Murthy, Spectrophotometric determination of uranium with anthranilic acid and rhodamine 6G, *Talanta* 27 (1980) 442–444.
- [16] J.L. Perez Pavon, B. Moreno Cordero, E. Rodriguez Garcia, J. Hernandez Mendez, Determination of uranium using a flow system with reagent injection. Application to the determination of uranium in ore leachates, *Anal. Chim. Acta* 230 (1990) 217.
- [17] Y. Ru, L. Yan, S. Guilan, W. Tao, P. Jiaomai, Spectrophotometric determination of uranium in natural water with the new chromogenic reagent *p*-carboxychlorophosphonazo, *Anal. Chim. Acta* 314 (1995) 95–99.
- [18] B.N. Murty, Y.V.S. Jagannath, R.B. Yadav, C.K. Ramamurty, S. Syamsundar, Spectrophotometric determination of uranium in process streams of a uranium extraction plant, *Talanta* 44 (1997) 283–295.
- [19] J.E. Currah, F.E. Beamish, Colorimetric determination of uranium with thiocyanate, *Anal. Chem.* 19 (1947) 609–612.
- [20] W.B. Smith, J. Drewry, Colorimetric determination of uranium in phosphate rock after extraction with alkyl acid phosphates, *Analyst* 86 (1961) 178–184.
- [21] S. Abe, H. Weisz, Rapid separation and determination of uranium(VI) by use of DEAE anion-exchange paper and the ring-oven technique, *Mikrochim. Acta* 58 (1970) 550–552.
- [22] S.C. Dubey, M.N. Nadkarni, Extractive spectrophotometric determination of uranium with malachite green, *Talanta* 24 (1973) 266–267.
- [23] K.C. Hughes, D.J. Carswell, Separation of the principal components in monazite, *Analyst* 95 (1970) 302–303.
- [24] C. Hartmann, J. Smeyers-Verbeke, W. Pinninckx, Y.V. Heyden, P. Vankeerberghen, D.L. Massart, Reappraisal of hypothesis testing for method validation: detection of systematic error by comparing the means of two methods or of two laboratories, *Anal. Chem.* 67 (1995) 4491–4499.
- [25] M.A. El-Ries, Spectrophotometric determination of piroxicam and tenoxicam in pharmaceutical preparations using uranyl acetate as a chromogenic agent, *Anal. Lett.* 31 (1998) 793–807.
- [26] S. Sadeghi, G.R. Dashti, M. Shamsipur, Lead-selective poly(vinyl chloride) membrane electrode based on piroxicam as a neutral carrier, *Sens. Actuators B* 81 (2002) 223–228.
- [27] V.V. Nalimov, *The Application of Mathematical Statistics to Chemical Analysis*, Pergmon Press, Oxford, 1963, pp. 167–189.
- [28] J. Mendham, R.C. Denney, J.D. Barnes, M. Thomas, *Statistics: Introduction to Chemometrics Vogel's Textbook of Quantitative Chemical Analysis*, sixth ed., Pearson Education, Singapore, 2002, p. 137.