Development of a simple spectrophotometric method to estimate uranium concentration in LiCl–KCl matrix

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Abstract

A fast, precise and simple spectrophotometric method was developed for the estimation of uranium in LiCl–KCl salt matrix using phosphoric acid as a complexing agent. The 421 nm absorbance peak of uranium was found to be spectral interference free and area of this peak was used for the quantitative analysis. Linearity over 100–7000 ppm with a detection limit of 25 ppm of uranium in 10% LiCl–KCl matrix was obtained by this method. The present method was successfully applied for the quantitative estimation of uranium in synthetic salt mixtures and the results were found to be more accurate than the values measured by ICP-OES.

Keywords Spectrophotometer · Uranium · LiCl–KCl · Phosphoric acid · Quantification

Introduction

To meet the increasing energy consumption, nuclear power is considered as one of the viable emission free energy sources in the world. In India, a huge demand for nuclear power can be fulfilled by the use of metallic fuels in fast reactors, which promises to have a high breeding ratio and lower doubling time [1]. For the reprocessing of the metallic fuel, pyrochemical processing is a viable method, which has several advantages over PUREX process [2–5]. The electrorefining process which uses LiCl–KCl as a eutectic salt was developed by Argonne National Laboratory for the reprocessing of U–Pu–Zr alloy fuel [5]. Lanthanides, alkali metals and alkaline earth metals are the major constituents of fission products remain in the salt along with some amount of uranium with other actinides. When the concentration of these elements present in salt exceeds

certain limits (~ 10 wt%), the salt must be purified before its reuse [6]. Salt purification allows recycling of the uranium and elimination of the fission products. The removal of fission products is generally done by treating the salt with zeolite ion exchange resins [7–9]. But prior to this, removal of uranium and other actinides is carried out by 'actinide drawdown' process [10]. The recovery of uranium from salt requires knowledge of uranium concentration present in the feed and outlet batches of salt phase. Therefore, determination of uranium concentration becomes a very important criterion to decide on the number of runs in the 'actinide drawdown' process. Around 99% of uranium is recovered from the salt phase by the above process [10].

There are various methods available in the literature for the estimation of uranium from percentage to ultra trace levels [11–20]. Direct determination of uranium is possible with Inductive Coupled Plasma (ICP) based mass spectrometry (ICP-MS) or atomic emission spectroscopy (ICP-AES) techniques [11, 12]. At low concentration of the matrix, these are reliable techniques and give accurate results; however, it is not possible to achieve accurate results when the matrix concentration is high and removal of the matrix is often required. Other techniques such as Neutron Activation Analysis (NAA) [15], electrochemical sensors [16], liquid scintillation counter [17], alpha spectrometer and XRF [18–20] can be used for uranium determination but these techniques require either complex sample preparation steps or sophisticated instruments. Photoluminescence

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is a very sensitive technique for the determination of uranium. Ultra trace luminescent detection of uranium can be achieved with the use of complexing agents such as phosphoric acid (H_3PO_4), sulphuric acid (H_2SO_4), and dipicolinic acid [21–24]. But in presence of matrix and other ions, the inherent problem of severe quenching restricts the use of luminescence spectroscopy as a technique for uranium determination. Due to its simplicity along with good precision and accuracy, spectrophotometric method is another alternate low cost technique for the determination of uranium. The major issue in determination of uranium by this method is the low sensitivity. The problem of low sensitivity can be overcome by the use of complexing agents such as resorcinol, arsenazo etc. Uranium can be detected at ppm level using these complexing agents [25–28].

The main objective of the present work is to develop a spectrophotometric based method for the quantification of uranium in molten salt, which can be easily adapted for real samples. However, handling of this salt and direct analysis require inert atmosphere due to hygroscopic nature of LiCl–KCl. In order to carry out the experiments in open atmosphere, the salt is dissolved in aqueous medium. The presence of salt broadens the absorbance peaks of uranium in aqueous medium by forming predominantly uranyl chloro complex. Broadening of peaks refrains one to use absorption spectroscopy as an analytical tool. To avoid the formation of chloro complexes, which is responsible for broadening of absorption peaks, different acids such as HCl, HNO_3, H_2SO_4 and H_3PO_4 are tried in the present work as complexing agents. Compared to all the acids, the broadening of peaks is found to be least in H_3PO_4 medium. Hence, H_3PO_4 medium is used for the estimation of uranium in LiCl–KCl matrix. The main advantage of the present method is that the accuracy of uranium estimation in the salt matrix is better than that of ICP-OES. Furthermore, the optical fibre based spectrophotometric determination of uranium will be useful in adapting the present method to pyro processing streams. Though, quantitative prediction of the lanthanides in LiCl-CsCl eutectic salt is available in literature [29], to the best of our knowledge there are no reports available for the uranium estimation in LiCl–KCl molten salts.

Experimental

Stock solution of uranium was prepared by dissolving the required amount of analytical grade UO_2 powder in hot distilled nitric acid and evaporated to dryness. The residue was then dissolved by adding water to get the required concentration of 23.8 mg/ml. The final concentration of uranium in stock solution was determined by ICP-OES. From this stock, solutions of different concentrations of uranium were prepared for further use. A stock solution of salt mixture

(45 wt% LiCl and 55 wt% KCl) was prepared by dissolving these salt chlorides (Loba Chemie, 99.9%) in water. It is to be noted that above 25 wt% of salt mixture was not completely soluble in aqueous medium and hence stock solution of salt mixture used in our experiments was restricted to 25 wt%. High purity (> 99.95%) rare earth oxides (La, Pr, Nd, Sm, Eu, Gd) and Y_2O_3 were procured from M/s Indian Rare Earths Ltd. and used for preparing their standard solutions. RbCl, CsCl, $SrCl_2$, $BaCl_2$ were purchased from M/s Sigma Aldrich and used as supplied for preparing their solutions. De-ionized water (18 MΩ) obtained from a Milli-Q (Millipore) system was used in the preparation of the above solutions. The H_3PO_4, H_2SO_4, HCl, HNO_3 used were Merck make of analytical grade.

UV–Vis spectra were recorded using a fiber optic spectrophotometer, model AvaSpec-2048 (300 lines per mm grating) in the range of 220–480 nm. AvaLight-DH-S module containing deuterium (78 W) and halogen lamp (5 W) is used as a light source in our experiment. Charge Coupled Device (CCD) based detector (2048 pixels) allows to record the spectrum within seconds (1.1 ms/scan). 10 mm path length fused silica cuvette (Sterna make) was used as the sample cell. All spectra were subtracted from blank which was recorded using identical experimental conditions without uranium present in the solution. All the measurements were carried out at room temperature. Luminescence spectra were recorded using Edinburgh spectrofluorimeter, model FLS920, with a 450 W Xe lamp as the excitation source. A band pass of 3 nm was set for both the excitation and emission monochromators. Solution for recording the luminescence spectra were taken in 10 mm path length fused silica cell. A long-wavelength pass filter, (UV-39, Shimadzu) with a maximum and uniform transmittance (> 85%) above 400 nm, was placed in front of the emission monochromator, to reduce the scatter of the incident beam into the emission monochromator.

Results and discussion

In the text the term 'salt mixture' is referred to 45 wt% LiCl and 55 wt% KCl. The 'other ions' is referred to the different elements as given in Table 1 with a total concentration of 8343 ppm.

Effect of salt on absorption spectrum of uranium

Figure 1a shows the absorption spectrum of 1000 ppm uranium in aqueous medium. The spectrum is over the range 350–450 nm and exhibits a structure having four major peaks at 393, 404, 415 and 427 nm. The four fingered feature is the characteristic signature of uranyl hydrate i.e. $UO_2(H_2O)_5^{2+}$, a uranium specie, exists in aqueous medium [30–32].

Table 1 Composition of the major elements ('other ions') present in 10% salt matrix

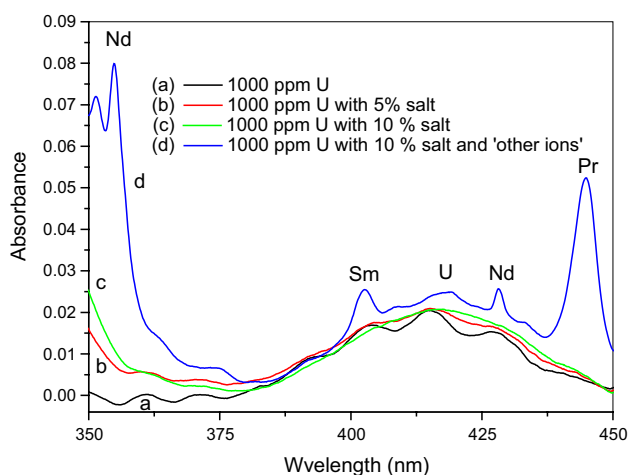| Element	Concentration (ppm)	Element	Concentration (ppm)
$LaCl_3$	829	YCl_3	394
$PrCl_3$	750	RbCl	194
$NdCl_3$	2700	CsCl	1300
$SmCl_3$	530	$SrCl_2$	590
$EuCl_3$	86	$BaCl_2$	920
$GdCl_3$	50	Total	8343

Fig. 1 Absorption spectra of **a** 1000 ppm U, **b** 1000 ppm U with 5% salt mixture, **c** 1000 ppm U with 10% salt mixture and **d** 1000 ppm U with 10% salt mixture and 'other ions' in aqueous medium

Figure 1b, c shows the absorption spectra of 1000 ppm uranium with the addition of 5 and 10% salt mixture in aqueous medium, respectively. It can be seen from the Fig. 1b that the absorption peaks of uranium is broadened with the addition of salt mixture and the peaks completely disappears at 10% salt concentration (Fig. 1c). The broadening of absorption peaks of uranium in the salt mixture could be due to the formation of chloro specie of uranium (UO_2Cl^+). Similar observation was reported by Runde et al. [33] for uranium absorbance in the presence of 1 M NaCl solution. Figure 1d shows the absorption spectra of 1000 ppm uranium with 'other ions' in the salt mixture in the region 350–450 nm. The reason for monitoring the absorption spectra in presence of 'other ions', will be discussed later. It can be seen from the figure that many absorption peaks appeared due to the presence of 'other ions'. The disappearance of characteristic features of uranium in the salt mixture and the appearance of other absorption peaks, quantification of uranium in aqueous medium becomes difficult in presence of 'other ions' without adding any complexing agent.

Effect of different acids on absorption spectrum of uranium in salt matrix

To find out a suitable ligand to bind with uranium, in presence of salt matrix, which should show characteristics absorption peaks of uranium, various acids such as HCl, HNO_3, H_2SO_4 and H_3PO_4 have been tried. Figure 2b, e shows the absorption spectra of 1000 ppm of uranium with 10% salt mixture in 1 M of HCl, HNO_3, H_2SO_4 and H_3PO_4, respectively. For comparison, absorption spectrum of 1000 ppm uranium with 10% salt mixture in aqueous medium (without any acid) is also shown in Fig. 2a. It can be seen from this figure that absorption spectrum of uranium in HCl and HNO_3 medium is broadened (Fig. 2b, c), which is similar to the spectra of uranium in aqueous medium (Fig. 2a) with a slight increase in absorbance. It is to be noted that even with the increase in concentration of these acids up to 3 M, spectra remain featureless. In 1 M HCl and HNO_3, broadening is due to the formation of UO_2Cl^+ and $UO_2NO_3^+$, respectively [34–36].

On the contrary, in the case of H_2SO_4 and H_3PO_4, the absorption spectra exhibit characteristic uranium peaks even in the presence of 10% salt mixture. The spectra exhibited four sharp peaks at 400, 411, 421 and 434 nm (Fig. 2d, e). Compared to the spectra in aqueous medium without salt mixture (Fig. 1a), the peak positions are red shifted by 7 nm in these media. The absorption peaks of uranium in H_2SO_4 medium also showed a similar shift [37]. The formed specie could be UO_2SO_4 in 1 M H_2SO_4 and $UO_2(HPO_4)$/ $UO_2(H_3PO_4)$ in 1 M H_3PO_4 [37, 38]. This indicates that though 10% salt is present, SO_4^{2-} and PO_4^{3-} ions coordinate strongly with uranium ion and replace Cl^- ion from the inner coordination sphere of uranium. This behavior of preferential coordination can be explained based on the basicity,
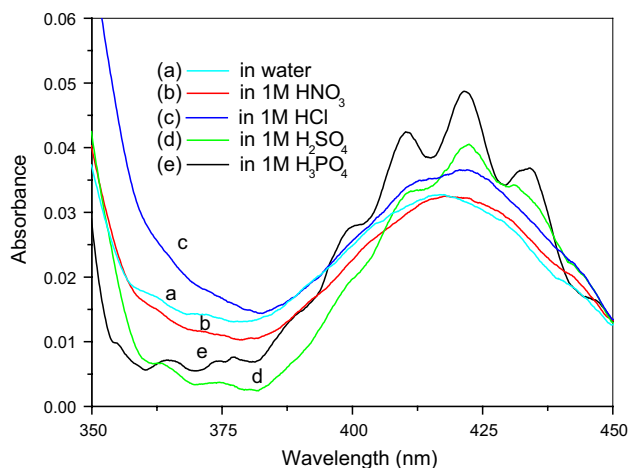
Fig. 2 Absorption spectra of 1000 ppm U with 10% salt mixture in **a** aqueous, **b** 1 M HNO_3, **c** 1 M HCl, **d** 1 M H_2SO_4 and **e** 1 M H_3PO_4

which increases in the order; $PO_4^{3-} > NO_3^- > SO_4^{2-} > Cl^-$. Though nitrate ions also can replace Cl^-, the featureless absorption spectra of $UO_2NO_3^+$ (Fig. 2b), disqualify HNO_3 medium for uranium analysis. In our studies, we have chosen H_3PO_4 medium because uranium absorption peaks are intense in this acid compared to H_2SO_4.

Effect of H_3PO_4 concentration on absorption spectrum

Figure 3 shows the absorption spectra of 1000 ppm of uranium with 10% salt as a function of H_3PO_4 concentration. It is to be noted that when the concentration of H_3PO_4 is below 0.5 M, LiCl–KCl salt mixture starts precipitating and hence salt concentration of 0.5 M and above were used for recording the spectra. Precipitation may be due to the formation of KH_2PO_4, which has a low solubility in dilute H_3PO_4 medium [39]. It can be seen from this figure that the absorbance of uranium at 421 nm is nearly the same for 0.5 and 1 M H_3PO_4 but there is a slight drop in the absorbance of uranium (~ 2%) for 2 M H_3PO_4. Hence, 1 M H_3PO_4 was used in subsequent experiments for the estimation of uranium.

Effect of salt on luminescence spectrum of uranium

H_3PO_4 has been widely used as a complexing agent for the determination of uranium by luminescence spectroscopy [21]. Luminescence technique can be used as an alternate method over spectrophotometry for the estimation of uranium in salt mixture. With this in mind, the luminescence spectrum of uranium in 1 M H_3PO_4 medium was recorded. Figure S1 shows the luminescence spectra of uranium with and without salt in 1 M H_3PO_4. To avoid the saturation of detector, t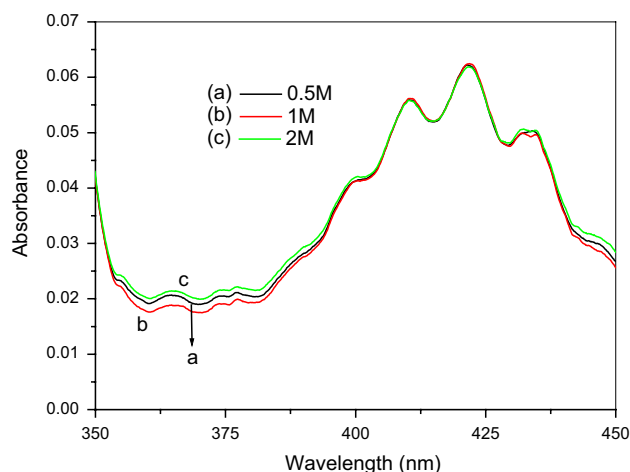he concentration of uranium has been brought down to 50 ppm. It can be seen that small amount of salt (0.25%) resulted in 98% decrease in the luminescence intensity of uranium. Therefore, estimation of uranium in salt matrix by luminescence method will lead to erroneous results.

Effect of 'other ions' on absorption spectrum of uranium with salt in H_3PO_4

As mentioned earlier that in pyro-reprocessing, apart from uranium, salt phase also contains other elements. Therefore, it is necessary to see the effect of these other elements on the absorption spectrum of uranium. The major elements given in Table 1 are present in salt mixture that is processed from nuclear fuel [6]. The concentration of rare earth ions presented in Table 1 correspond to the one referred in the electrorefining bath of an experimental breeder reactor (EBR-II) [40]. The concentration of 'other ions' are given in this Table corresponds to 10% salt mixture. Figure 4b shows the absorption spectra of 1000 ppm uranium with 10% salt mixture along with 'other ions' in 1 M H_3PO_4. For comparison the absorption spectrum of 1000 ppm uranium with 10% salt mixture but without 'other ions' is illustrated in Fig. 4a. It can be seen from Fig. 4b that extra peaks appear due to the absorbance of some elements present in 'other ions'. In order to identify these peaks, each element present in 'other ions' was sequentially added to the solution and the absorbance spectra were recorded. It was found that except Pr, Nd and Sm, no other elements gave rise to any absorption peaks in the region 350–450 nm. The two absorption peaks found at 355 and 428 nm are due to Nd. The peaks observed at 402 and 444 nm are due to Sm and Pr, respectively. From this
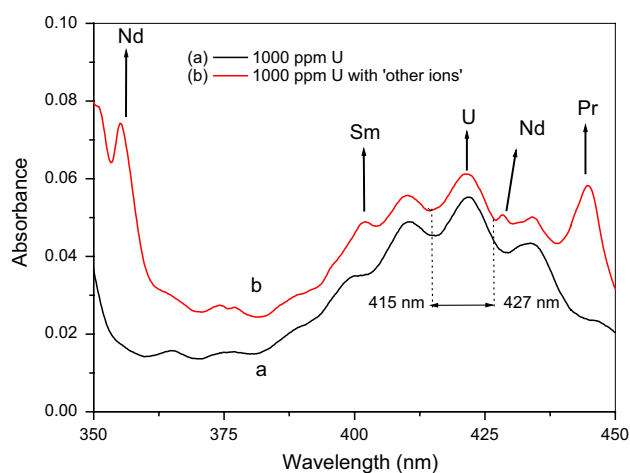

Fig. 3 Absorbance spectra of 1000 ppm U with 10% salt mixture as a function of H_3PO_4 concentration **a** 0.5 M, **b** 1 M and **c** 2 M

Fig. 4 Comparison of absorption spectra of 1000 ppm U with 10% salt mixture without (**a**) and with (**b**) 'other ions' in 1 M H_3PO_4. Peak area between (415 and 427 nm) has been considered for uranium analysis (arrows)
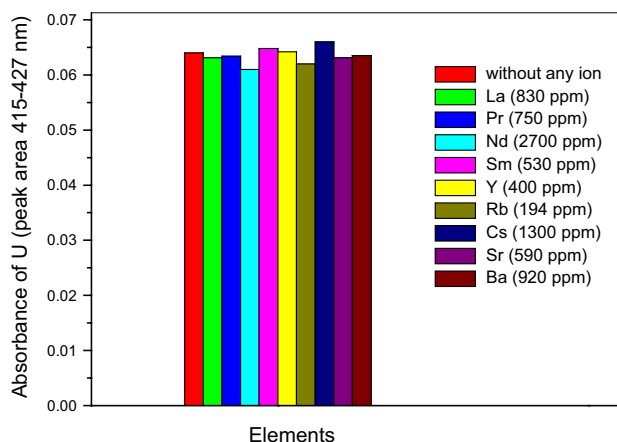
Fig. 5 Bar graph showing the influence of other elements on the uranium (1000 ppm) absorbance with 10% salt mixture in 1 M H_3PO_4

Fig. 6 Plot of absorbance at 421 nm (peak area) as a function of uranium concentration with **a** 0%, **b** 10% and **c** 14% salt mixture in 1 M H_3PO_4

Fig. 4b, it is clear that the interference due to the 'other ions' to the absorption peak of uranium at 421 nm is minimum and the area of this peak over 415–427 nm can be considered for the quantitative analysis. Due to the presence of high concentration of 'other ions' (~ 8343 ppm) the incident light gets scattered, which increases the background absorbance (Fig. 4b). Figure 5 shows the influence of major elements found in 'other ions' on the absorption peaks area (415–427 nm) of uranium. It can be seen that peak area over 415–427 nm is not much influenced by the presence of these elements. About 1–4% variation in the area was observed. The above exercise clearly tells that absorption spectroscopy can be used for the estimation of uranium in presence of other elements in salt matrix using 1 M H_3PO_4.

Calibration curve and detection limit

The area (415–427 nm) under the absorption peak maximum of uranium at 421 nm in 1 M H_3PO_4 shows a linear relationship to the uranium concentration in the range 100–7000 ppm (Fig. 6a). To see the effect of salt on calibration graph, experiments were also carried out in presence of salt mixture. Figure 6b, c show the calibration plots of uranium with 10% and 14% salt mixtures. Due to the presence of salt, the calibration plots showed a slight decrease in slope. The slope (Fig. 6c) was found to be decreased by 3% when 14% salt mixture was present as compared to the slope without salt (Fig. 6a). This clearly implies that the salt matrix of up to 14% does not affect the calibration plot of uranium to a large extent. Regression coefficient (R^2) values of linear fitting were found to be greater than 0.997. The detection limit (3σ) of uranium was estimated to be 25 ppm in 10% salt mixture.
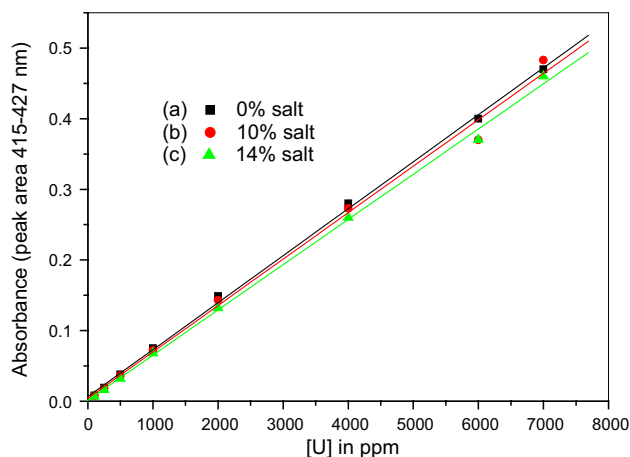
Quantitative analysis

Three synthetic solutions containing different concentrations of uranium and salt mixture are prepared and treated as unknown samples (Table 2). 'Other ions' (as per Table 1) were also added in these solutions as these are the major elements found in salt phase. The samples were diluted before analyzing and H_3PO_4 was also added to these samples. The final concentration of salt mixture and H_3PO_4 was 10% and 1 M, respectively. The absorbances at 421 nm (in terms of peak area) of these solutions were then measured and the concentrations of uranium in these samples were obtained from the calibration curve (Fig. 6b). Concentrations were also obtained from the calibration curve plotted without salt matrix (Fig. 6a). It can be seen from the Table 2 that relative error in the measured values obtained from the matrix matched calibration curve (Fig. 6b) is ~ 2.5% whereas error is slightly more (4–7%) if one uses the standard curve without matrix (Fig. 6a). From the Table 2 it is clear that the results obtained by the present method are more consistent with the actual value. For the ICP-OES analysis, the samples were diluted in such a way that the final concentration of uranium is in the range of 20–50 ppm. The analysis by ICP-OES gave higher values for all the three synthetic samples. This may be due to the presence of high content of salt mixture and other elements which probably enhance the uranium emission line intensity by adding background signal. The value of relative standard deviation (RSD) in the estimates by the present method was less than 1% (5 replicates) whereas by ICP-OES it was 5%. It is to be noted that CCD based spectrophotometer records the spectrum within seconds and so the present method allows the overall analysis time to be < 10 min. Furthermore, the 'simplicity' of the method arises because of the use of simple chemical

Table 2 Comparison of the actual and measured concentration of uranium in salt mixture

Sample ID*	Concentration as prepared		Concentration of U (ppm) as measured		
			Present method[a]		ICP-OES[b]
	[U] ppm	[Salt] %	(Using calibration without salt)	(Using calibration plot with 10% salt)	
Syn1	820	17	765 (− 6.7%)	841 (+ 2.5%)	950 (+ 15%)
Syn2	1194	17	1124 (− 5.9%)	1181 (− 1.1%)	1360 (+ 14%)
Syn3	11,940	11	12,515 (+ 4.8%)	12,200 (+ 2.2%)	13,580 (+ 14%)

Relative error in measured value is shown in parenthesis

*Other elements are also added in all three samples as per Table 1

[a]RSD-1%

[b]RSD-5%

reagents, no synthesis/separation process and does not require sophisticated instruments.

Conclusion

A fast, precise and accurate method has been developed for the estimation of uranium in LiCL–KCl salt matrix with H_3PO_4 (1 M) as a complexing agent. Validation of the method was carried out by estimating uranium concentration in three synthetic samples containing known amount of uranium, 'other ions' and salt mixture. Present study shows that this method is more accurate and superior to the values obtained from ICP-OES. This study has demonstrated that the estimation of uranium in presence of salt mixture is possible without any separation. Uranium can be estimated with an accuracy of 7% using standard calibration curve and < 3% with matrix matched calibration. Limit of detection has been shown to be about 25 ppm in 10% salt mixture (0.025 wt%), which is about nearly ten times less than that found in real samples. Fibre optic coupled UV–Vis technique to estimate uranium in salt matrix makes it attractive for application in nuclear industry.

Supplementary information

Luminescence spectra of uranium without and with salt in 1 M H_3PO_4 is given in the electronic supplementary information.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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