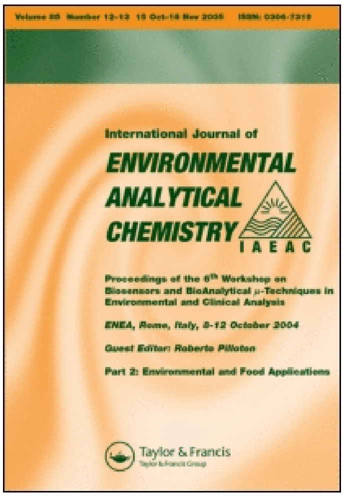

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# Separation and preconcentration of uranium(VI) from aqueous samples using a surfactant-coated alumina modified with meloxicam

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# Separation and preconcentration of uranium(VI) from aqueous samples using a surfactant-coated alumina modified with meloxicam

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A new simple and reliable method for the separation, and preconcentration of trace levels of $UO_2^{2+}$ ions from water samples is developed using a modified sodium dodecyl sulphate (SDS) coated alumina solid phase. The effects of pH, flow rate of sample solution, and foreign ions on the sorption of uranium have been investigated. Twenty micrograms of $UO_2^{2+}$ ions from 1000 mL (pH 5) of aqueous phase could be quantitatively extracted into 1.5 g of meloxicam modified SDS coated alumina. The preconcentration could be made selective to $UO_2^{2+}$ ions by using EDTA as masking agent for transition metal ions and Th(IV). The collected $UO_2^{2+}$ ions were eluted out with 2 mL of HCl solution (1 M) and determined spectrophotometrically using arsenazo(III) as chromogenic reagent. The detection limit corresponding to three times the standard deviation of the blank was found to be $0.52\,\mu g\,L^{-1}$. The relative standard deviation for recovery of $1.0\,\mu g\,L^{-1}$ of $UO_2^{2+}$ ions from water sample (1000 mL) was 3.2% ($n = 5$). The proposed method was used for the separation of uranium ions from various water samples.

**Keywords:** uranium; preconcentration; SDS coated alumina; meloxicam

## 1. Introduction

Quantitative analysis of uranium in water and biological samples at very low concentration is still difficult and this problem can be solved by coupling preconcentration and separation procedures with analytical techniques. By performing the preconcentration process the ratio of the amount of a desired trace element to that of the original matrix is converted into a new matrix which is suitable for analytical determination and also preconcentration improves the analytical detection limit by increasing the sensitivity up to several orders of magnitude, enhances the accuracy of the results, offers a high degree of selectivity and facilitates calibration [1,2].

In recent years, solid phases modified with the immobilised organic compounds are attracting great interest because of high selectivity, high enrichment capacity and operational simplicity. In solid phase extraction (SPE) [3], immobilisation of organic ligands on the surface of inorganic or organic solid supports is aimed to modify the surface with certain target functional groups that can be exploited for further analytical purposes. A number of solid sorbents such as neutral polymer-Amberlite

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XAD series [4], silica [5], octadecyl silica membrane discs [6–8], activated silica gel [9], controlled pore glass [10], polyurethane foam [11], activated carbon [12] and cationic or anionic exchange resins [13–23] have been reported for the enrichment of uranium(VI) from dilute solutions prior to determination by a variety of analytical techniques.

It is well understood that, in an acidic medium, sodium dodecyl sulphate (SDS) as anionic surfactants is sorbed on the positively charged alumina surface to form aggregates [24,25]. Hydrophobic chelating agents were immobilised into micelles and the produced system can be used for separation or preconcentration of various metals such as iron [26], cobalt [27], chromium [28], mercury [29] and lead [30] from aqueous samples.

Meloxicam (4-hydroxy-2-methyl-*N*-(5-methyl-2-thiazolyl)-2H-1,2-benzothiazine-3-carboxamide-1,1-dioxide (MLC) (see Figure 1)) is a non-steroidal anti-inflammatory drug. It is insoluble in water and has been shown to have the tendency to form metal cation complexes in a non-aqueous medium [31,32].

In the present work, MLC was immobilised on SDS coated alumina. Then, the produced modified alumina was used for the selective preconcentration of uranium from a large volume of aqueous samples. The spectrophotometric method based on arsenazo(III) [33,34] was used for the determination of uranium after the complete desorption of $UO_2^{2+}$ ions with hydrochloride acid as a suitable eluent. To the best of our knowledge, there is no report about the preconcentration of uranyl ions using MLC in the literature.

## 2. Experimental

### 2.1 *Reagents*

Analytical reagent-grade chemicals and doubly distilled water were used. Pure meloxicam were obtained from Sigma (St. Louis, MO, USA). Sodium dodecyl sulphate (SDS), $\gamma$-type alumina, $UO_2(NO_3)_2$ and arsenazo(III) were purchased from E. Merck (Darmstadt, Germany) and used without further purification. Millipore filters were prepared from FILALBERT S. L. (Barcelona, Spain). Working solutions were prepared from the stock solution by serial dilutions with doubly distilled water.

### 2.2 *Apparatus*

A Pharmacia LKB 4054 spectrophotometer (Pharmacia, Sweden) equipped with 10 mm matched silica cells was used for absorbance measurements. A WTW Multilab 540

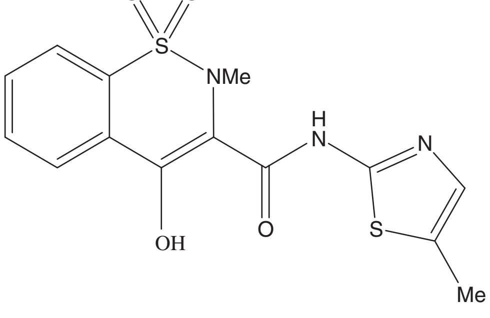

Figure 1. The structure of meloxicam (MLC).

Ionalyzer pH/mV meter (WTW, Weilheim, Germany) with a combined glass pH electrode was used for pH measurements. The flow of the sample through the column was adjusted with a vacuum pump model C55JXHRL-4205 (J/B Industries Inc., Aurora, USA).

### 2.3 *Preparation of solid-phase extraction particles*

Purified $\gamma$-type alumina particles (1.5 g) and 80 mg of SDS were suspended in 75 mL of water and then mixed with 25 mL of a solution containing 2.0 mg of MLC and 20 mg SDS. The suspension was acidified (pH $2.5 \pm 0.1$) with hydrochloric acid solution (1.0 M) and stirred for 15 min. After removing the supernatant solution, MLC-SDS coated alumina particles were transferred to a Millipore filter holder for preparation of the extraction column (15 mm in height × 5 mm in diameter). The column was washed with 10–50 mL of double distilled water for the removal of free $H^+$ ions. A 0.45 µm Millipore filter was inserted between the packed column and a sintered glass disk to prevent the disk from clogging.

### 2.4 *Solid-phase extraction of $UO_2^{2+}$*

After the preparation of extraction column, 50–1000 mL of water samples containing uranyl ions (pH 5) were passed through the column at a flow rate of $1 \pm 0.1\ \mathrm{mL\,min^{-1}}$. The adsorbed uranyl ions were eluted from the column with 2 mL of 0.1 M hydrochloric acid and collected in a test tube. The eluent was transferred to a 50 mL beaker and evaporated to near dryness on a hotplate. Then 5 mL of hydrochloric acid (6 M) and 0.3 g of zinc powder were added to the residue to reduce U(VI) to U(IV). During the reduction process, the beaker was carefully shaken to dissolve all of the zinc. Immediately, 1.5 mL of 0.63 M oxalic acid and 0.5 mL of arsenazo(III) solution (0.2% w/v) was added. After 15 min, the absorbance of the violet-blue colour of the uranium-arsenazo(III) complex was measured at 664 nm against a reagent blank solution.

## 3. Results and discussion

Recently, the use of organic modifiers with large adsorption capacity and high selectivity in SPE of uranium as uranyl ions has been lionised [9,15,34]. So, in continuation of our works on SPE using $Al_2O_3$-SDS [35], we were interested to evaluate the behaviour of modified $Al_2O_3$-SDS with MLC for preconcentration and determination of uranyl ions from aqueous samples. It must be noted that the complexation reactions between MLC and some metal ions have been reported in the literature and it was found that MLC can form high stable complexes with the uranyl ions [36,37].

In preliminary experiments, the interaction between MLC and $UO_2^{2+}$ ions was investigated by recording the UV-Vis spectra of $1 \times 10^{-4}$ M of MLC and uranyl ions and also their 1 : 1 mixture in acetonitrile. The resulting spectra are shown in Figure 2. As can be seen the formed complex between $UO_2^{2+}$ and MLC shows an absorption spectrum which is quite differ from MLC and $UO_2^{2+}$ individual absorption spectra. The composition of the formed complexes was determined by mole-ratio method ($\lambda = 400$ nm) and indicated a 1 : 2 reaction between MLC and $UO_2^{2+}$ ions.

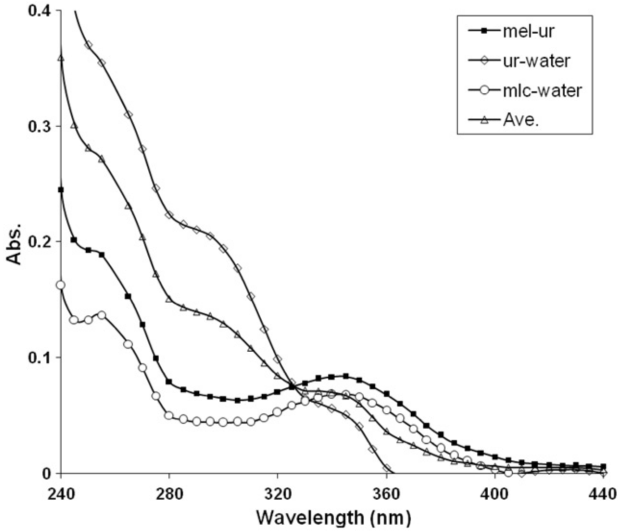

Figure 2. Absorbtion spectra of (Δ) $1 \times 10^{-4}$ M uranyl ions (○) $1 \times 10^{-4}$ M MLC (■) $1 \times 10^{-4}$ M of $UO_2^{2+}$-MLC complex in acetonitrile and (◇) calculated spectra of uranyl ions with MLC without any interaction.

As mentioned above, when the acidified solution of SDS and MLC is shaken in the presence of alumina powder, hemi micelle or admicelle forms of SDS is adsorbed on protonated alumina and traps the MLC molecules. The adsorption of $UO_2^{2+}$ ions on different sorbents, which were prepared using $Al_2O_3$, $Al_2O_3$-SDS and MLC-SDS-$Al_2O_3$ was studied by passing 250 mL of uranyl solution (40 μg $L^{-1}$, pH = 5) through the prepared columns and then eluted with 2 mL of 1 M HCl solution. The amounts of uranyl ions in eluent solutions were determined with arsenazo(III) method. The obtained results are summarised in Table 1. As can be seen, while no considerable quantity of uranyl ions are adsorbed on bare alumina and $Al_2O_3$-SDS particles, nearly all of the uranyl ions are adsorbed on the MLC-SDS-$Al_2O_3$ column. It was observed that the chemically immobilised MLC formed a stable complex with $UO_2^{2+}$ ions at pH 5.0, so that the colour of MLC-SDS-$Al_2O_3$ particles was changed from bright yellow to deep yellow.

### 3.1 *Effect of MLC immobilised amounts on SDS-coated alumina*

In all experiments the concentration of SDS was fixed approximately at 2 mg $mL^{-1}$, which is below the critical micelle concentration (CMC) of SDS ($8 \times 10^{-3}$ M). Above the CMC, micelle aggregates are formed and do not adsorb on alumina surface. To examine the effect of immobilised MLC amounts on the adsorption of $UO_2^{2+}$ ions, several sorbents were prepared using 1.5 g alumina, 100 mg SDS and different amount of MLC and their ability in extraction of 20 μg of uranyl ions from 250 mL water samples were evaluated (Table 1). As can be seen, by using 2 mg of MLC, all of $UO_2^{2+}$ ions are quantitatively extracted and a decrease in recovery values was observed by decreasing the amount of MLC. Therefore, 2 mg of MLC was used for the modification of SDS-$Al_2O_3$ in further experiments.

Table 1. Comparison of different sorbents for extraction of $UO_2^{2+}$ ions.

| Sorbent | Extraction (%) |
|---|---|
| $Al_2O_3$ | 10.0 ± 3.6 |
| $Al_2O_3$-SDS | 15.1 ± 2.5 |
| $Al_2O_3$-SDS-MLC (0.5 mg) | 42.3 ± 2.7 |
| $Al_2O_3$-SDS-MLC (1 mg) | 96.1 ± 2.2 |
| $Al_2O_3$-SDS-MLC (2 mg) | 98.6 ± 2.4 |
| $Al_2O_3$-SDS-MLC (3 mg) | 98.8 ± 2.4 |

Notes: Conditions: uranyl concentration: 80 μg $L^{-1}$; sample volume: 250 mL (pH 5); eluent: 2 mL of 1 M HCl; flow rate: 1 mL $min^{-1}$.

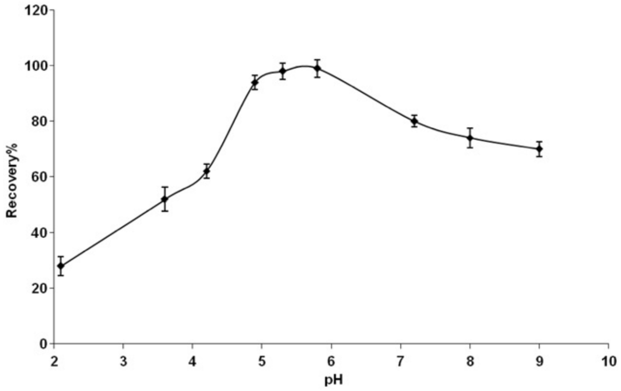

Figure 3. Effect of pH on the recovery of $UO_2^{2+}$ ions.
Notes: Conditions: uranyl concentration: 200 μg $L^{-1}$; sample volume: 100 mL; eluent: 2 mL of 1 M HCl; flow rate: 1 mL $min^{-1}$.

### 3.2 *Effect of pH on sorption of uranyl ions*

In solid phase extraction studies, pH is an important parameter for quantitative recovery of analytes [25]. The effect of pH on the extraction of uranyl ions was investigated in the pH range of 2 to 9. The adjustments of pH of the solutions were performed by using dilute NaOH or HCl (0.01 M). The results obtained are shown in Figure 3. The progressive decrease in the adsorption of $UO_2^{2+}$ ions at pH < 4.5 is probably related to weak complex formation between $UO_2^{2+}$ and immobilised MLC. Since MLC is easily dissolved in higher pH, so a mild decrease in recovery values at pH > 6 is probably resulted from desorption of immobilised MLC in these conditions. Therefore, in all experiments, pH 5 was chosen for the quantitative separation and preconcentration steps. It must be mentioned that the adjustments of pH 5 using acetate buffer (0.01 M) instead of HCl or NaOH had no effect on recovery values of uranyl ions.

### 3.3 *Effect of flow rate*

The influence of flow rates of the sample solution on the extraction of $UO_2^{2+}$ ions was investigated by passing 250 mL of sample solutions (40 μg $L^{-1}$ of $UO_2^{2+}$ ions) followed by

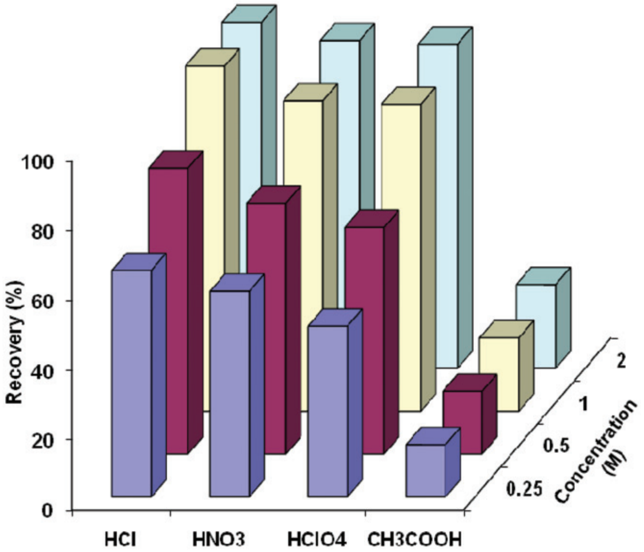

Figure 4. Influence of nature and concentration of acidic eluents on recovery of $UO_2^{2+}$ ions.
Notes: Conditions: uranyl concentration: 200 μg $L^{-1}$; sample volume: 100 mL (pH 5); eluent: 2 mL of 1 M HCl; flow rate: 1 mL $min^{-1}$.

elution of the column with 2 mL of 1.0 M HCl at a flow rate of 2 mL $min^{-1}$. The obtained recovery values at different sample flow rates in the range of 0.5 to 5 mL $min^{-1}$ were studied and the obtained results show that in high flow rates the recovery of $UO_2^{2+}$ ions diminishes most probably due to slow complexation reaction between MLC and uranyl ions and reaches maximum values at low flow rate. So, due to the importance of extraction time, a flow rate of 1 mL $min^{-1}$ was chosen for the sorption and stripping steps in further experiments.

### 3.4 *Elution of uranium from the column*

The nature and concentration of eluents have an important effect on desorption of uranium from the extraction column. Therefore, the elution of $UO_2^{2+}$ ions by various concentrations of mineral acids such as HCl, $HNO_3$, $HClO_4$ and $CH_3COOH$ were examined. The obtained results are shown in Figure 4. As can be seen among the tested reagents, HCl (1.0 M) was suitable for elution of $UO_2^{2+}$ ions from the extraction column. Also the influence of eluent volume was studied and it was observed that 2 mL of HCl (1.0 M) completely desorbed $UO_2^{2+}$ ions from column and increasing the eluent volume only decreased the preconcentration factor.

### 3.5 *Effect of foreign metal ions*

The recovery of $UO_2^{2+}$ ions in the presence of foreign ions was investigated. The obtained results indicated that except for $Ag^+$ and $Th^{4+}$, there is no considerable decrease in recoveries of $UO_2^{2+}$ ions. The tolerance limit was set as the amount of ion required to cause

Table 2. Recovery of $UO_2^{2+}$ ions from water solutions containing other cations.

| Interfering ion | Added as | Tolerance limit (mg cation) |
|---|---|---|
| $Na^+$ | NaCl | 31.2 |
| $K^+$ | KCl | 30.1 |
| $Ag^+$ | $AgNO_3$ | 1.1 |
| $Ba^{2+}$ | $BaCl_2$ | 2.2 |
| $Ca^{2+}$ | $CaCl_2$ | 10.1 |
| $Mg^{2+}$ | $MgCl_2$ | 6.5 |
| $Al^{3+}$ | $Al_2(SO_4)_3$ | 5.5 |
| $Fe^{3+}$ | $Fe(NO_3)_3$ | 4.5 |
| $Cr^{3+}$ | $Cr(NO_3)_3$ | 3.4 |
| $Cd^{2+}$ | $Cd(NO_3)_2$ | 4.6 |
| $Hg^{2+}$ | $Hg(NO_3)_2$ | 3.7 |
| $Co^{2+}$ | $Co(NO_3)_2$ | 4.1 |
| $Pb^{2+}$ | $Pb(NO_3)_2$ | 6.2 |
| $Ni^{2+}$ | $Ni(NO_3)_2$ | 3.7 |
| $Zn^{2+}$ | $Zn(NO_3)_2$ | 7.5 |
| $Th^{4+}$ | $Th(NO_3)_4$ | 0.9 |

Notes: Conditions: uranyl concentration: $20\,\mu g\,L^{-1}$; sample volume: 1000 mL (pH 5); eluent: 2 mL of 1 M HCl; flow rate: $1\,mL\,min^{-1}$.

a ±3% error in the recovery values of 20 μg uranyl ions (Table 2). As seen, the proposed method is free from interference from a large number of transitions, non-transition cations at high concentration ranges (about milligrams). Since the presence of EDTA had no effect in the determination of uranium, it can be used as a masking agent for other metal ions, when they are present along with uranium in large concentrations. The interfering effect of $Ag^+$, $Co^{2+}$, $Pb^{2+}$, $Zn^{2+}$, $Hg^{2+}$ and $Cd^{2+}$ was removed by using EDTA (1 mL of 1% EDTA solution) and $Fe^{3+}$ was masked by adding 5 mL of triethanolamine solution (10% w/v) during the adsorption step.

It is worth noting that no decrease in recovery values was observed for uranyl ions in the presence of various anions at the milligram levels.

### 3.6 *Study of preconcentration factor*

To determine the preconcentration factor, different volumes of sample solutions containing 10 μg $UO_2^{2+}$ were passed through the column and washed with 2 mL of 1.0 M hydrochloric acid (Figure 5). As seen, there are no considerable changes in recovery values with changing the volume of sample solution up to 1000 mL. Therefore, a preconcentration factor of 500 can be achieved. The obtained relative standard deviations of uranium recoveries under optimal conditions for five replicate measurements at 1.0 to $20\,\mu g\,L^{-1}$ levels were 3.2% and 2.4%, respectively. It must be noted that each prepared column can be used 20 times for quantitative recovery of uranyl ions without any regeneration. The capacity of proposed MLC-SDS-$Al_2O_3$ solid phase on sorption of $UO_2^{2+}$ ions was found to be $12.1\,mg\,g^{-1}$ of solid phase. This indicates that the column is capable of adsorption of large amounts of $UO_2^{2+}$ ions.

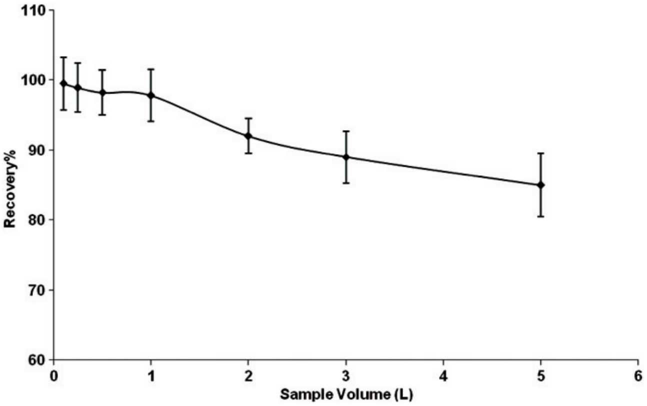

Figure 5. Recovery of 10 μg uranium from different sample volumes.
Notes: pH 5; eluent: 2 mL of 1 M HCl; flow rate: 1 mL min$^{-1}$.

Table 3. Results of $UO_2^{2+}$ recovery from 1000 mL (pH 5) of natural water samples.

| Sample (1000 mL) | Added (μg) | Found (μg)[a] | RSD (%)[b] |
|---|---|---|---|
| Tap water | – | ND[c] | – |
| | 2.0 | 2.11 (±0.05) | 2.37 |
| | 5.0 | 5.16 (±0.11) | 2.13 |
| Shahrchai river (Urmia, Iran) | – | ND[c] | – |
| | 2.0 | 1.99 (±0.06) | 3.01 |
| | 5.0 | 5.1 (±0.14) | 2.74 |

Notes: [a]Average of five determinations; [b]Relative standard deviation; [c]Not detected.

### 3.7 *Analytical applications*

To assess the applicability of the method to real samples, it was applied to the extraction, preconcentration and determination of uranium from water samples. A 1000 mL aliquot of water sample was adjusted to pH 5 and after adding sufficient amounts of masking agents, $UO_2^{2+}$ ions were concentrated and extracted using the proposed column and determined by the procedure described above. The uranium content equivalent to $UO_2^{2+}$ ions was obtained by the standard addition method and the results are shown in Table 3. The limit of detection (LOD) of the proposed method for determination of $UO_2^{2+}$ ions based on $3\sigma$ of the blank is 0.52 μg L$^{-1}$.

The analytical performance characteristics of the proposed sorbent are summarised in Table 4 and compared with some of other reported uranium sorbents in the literature [7,12,15,19–23,38–41]. As can be seen, the method proposed in this work, using the MLC-SDS-$Al_2O_3$ system for the preconcentration of uranyl ions, showed a low or similar LOD in most cases, or even superior in some cases, to the previously reported methods. Also, the proposed sorbent has a larger or similar capacity in comparison to some reported sorbents. Its low cost and simplicity as well its high selectivity for uranyl ions are important features of the MLC-SDS-$Al_2O_3$ system.

Table 4. Comparative data from some solid phase extraction studies on $UO_2^{2+}$ ions preconcentration.

| Ref. | Sorbent | Chelating agent | Retention/sorption capacity (mg g$^{-1}$ of SPE) | Linear range (μg L$^{-1}$) | LOD[a] | % RSD |
|---|---|---|---|---|---|---|
| [7] | Octadecyl silica membrane discs | Tri-*n*-octyl-phosphine oxide | 4.03 | 200–6000 | 100 ng L$^{-1}$ | 1.5 |
| [12] | Activated carbon | Diarylazobisphenol | 18.35 | 5–200 | 5 μg L$^{-1}$ | 2.5 |
| [15] | Amberlite XAD-4 | Succinic acid | 12.3 | 5–200 | 2 μg L$^{-1}$ | 2.5 |
| [18] | Duolite XAD761 | 9-Phenyl-3-fluorone | – | – | 4.5 ng L$^{-1}$ | 4.5 |
| [19] | Amberlite XAD-16 | 1,2-Dihydroxy arsinoyl phenylamino)methyl] phosphonic acid | 59.5 | 5–50 | 18–23 ng mL$^{-1}$ | 4.9 |
| [20] | Amberlite XAD-2 | Pyrogallol | 6.71 | 40–200 | 1.0 ng mL$^{-1}$ | 7.0 |
| [21] | Merrifield chloromethylated resin | Di-bis(2-ethylhexyl) malonamide | 62.5 | – | 20 ng mL$^{-1}$ | 5.2 |
| [22] | Merrifield peptide resin | 11,23-Disemicarbazono-26,28-*n*-dipropoxy-25,27-dihydroxy calix[4]arene | 3.09 | 100–1000 | 10 ng mL$^{-1}$ | 2.0 |
| [23] | Merrifield chloromethylated resin | Quinoline-8-ol (HQ) | 120.3 | 5–2000 | 5 μg L$^{-1}$ | 2.5 |
| [38] | Naphthalene | 5,7-Dichloroquinoline-8-ol | 1.88 | 2–100 | 2 ng mL$^{-1}$ | 1.5 |
| [39] | Naphthalene/ benzophenone | (2-Pyridylazo)-2-naphthol | 2.34 | 2–100 | 2 μg mL$^{-1}$ | 2.1 |
| [40] | Silica gel | Catechol | 15.94 | 2–100 | – | 1.4 |
| [41] | AXAD-16-3, 4-dihydroxy benzoyl methyl phosphonic acid | – | 1.66 | 2.5–25 | 10 ng L$^{-1}$ | 3.9 |
| This work | SDS coated alumina | Meloxicam | 12.1 | 1–20 | 0.52 μg L$^{-1}$ | 3.2 |

Note: [a]Limit of detection.

## 4. Conclusion

The proposed method for solid phase extraction of uranyl ions based on MLC-SDS coated alumina phase is very simple, economic, reproducible and selective. The reliable results obtained from each prepared column after 20 uses without any regeneration by MLC or SDS is an important advantage of the proposed MLC-SDS-$Al_2O_3$ solid phase. Due to the relative high preconcentration factor, traces of uranyl ions at ppb level can be accurately determined. The proposed method is free from interference for a large number of diverse ions, which are associated with uranyl ions in various samples.

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