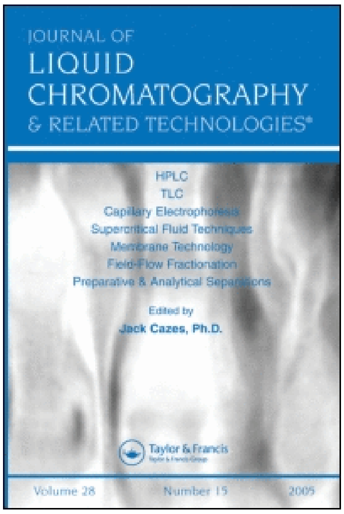

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Influence of the Lipophilicity of an Ion-Pairing Reagent on Metal Ion Separation using Ion-Pair HPLC

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Influence of the Lipophilicity of an Ion-Pairing Reagent on Metal Ion Separation using Ion-Pair HPLC

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Abstract: Tetraalkyl ammonium salts (TAAS) of a wide range of lipophilicities are used as ion-pairing reagents for simultaneous separation of proposed anionic metal complexes $[M(H_2PO_4)_3]^-$ of U(VI), Fe(III), and neutral Cu(II) using reversed-phase ion pairing high performance liquid chromatography (RPIP-HPLC). Tetramethylammonium bromide, tetraethyl ammonium chloride, and tetrapropyl ammonium bromide, due to their low hydrophobicities, are unable to separate U(VI) and Fe(III). Tetrabutyl ammonium perchlorate has separated the three metal ions. Tetrahexyl ammonium bromide, tetraheptyl ammonium bromide, and tetraoctyl ammonium bromide have enhanced resolution for the metal ions, but analysis time was prolonged due to the strong retention of nitrate ion. Also, equilibration time with the stationary phase increases with the increase in carbon atoms in the IPR. The potential of varied carbon containing IPRs has been compared for the analysis of U(VI) in simulated standards. The detection limit and RSD for Cu, Fe, and U are 2, 0.5, and 2 ppm and 4, 5, and 3.3%, respectively.

Keywords: Lipophilicity, Ion pairing, Metal ions, HPLC

INTRODUCTION

Ion-pair chromatography (IPC), as adapted to modern LC, is a versatile technique for inorganic and organic analysis.[1] IPC can be carried out in

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normal and reversed phase modes; each one has its own advantages.[2,3] Tetraalkyl ammonium salts (TAASs) are frequently used for ion pairing with negatively charged metal complexes and for certain anions.[4–7] Various mechanisms for solute retention in IPC have been proposed.[8] The optimization of the IPC involves the investigation of pH, organic modifier, concentration of ion pairing reagent and its lipophilicity, nature of the buffering salt, and type of stationary phase.[9] The most important factor in selection of a counter ion for a particular separation under consideration is its charge compatibility.[10–17] In principle, a single ion pairing reagent can be used for the optimization of separation and selectivity, provided that its adsorption covers a sufficiently wide range.[18] Changing the length of the alkyl chain readily alters the lipophilic character of these ions and, thus, a manipulation of the capacity ratio will be achieved by the alteration of the extraction constant.[19] Also, the nature and concentration of organic modifier greatly influences the adsorption of ion pairing reagents due to their degree of polarity.[20,21] A rule of thumb calls for the replacement of the pairing ion with a more lipophilic ion when sufficient retention shift is not observed. Popular choices tend to favor the relatively less lipophilic reagents regarding analysis time.[21] Bartha et al. have summarized their recommendations for the different chain length IPRs and methanol concentration combination for alkyl sulfonate and tetraalkyl ammonium ions.[22] The counter ion should be ideally univalent, aprotic, and soluble in the mobile phase, and must not undergo aggregation or secondary equilbria.[19] Alkyl ammonium ions meet almost all of these requirements in an environment having a high dielectric constant.

In the present investigation, potential use of symmetrical TAASs has been explored, regarding monitoring of metal ions of high environmental concern, such as copper and uranium. The main source of U in the environment is in the burning of fossil fuels. It is estimated that, annually, around 23 kg of U(VI) and 46 kg of Th(IV) are emitted by a particle suppressor 1,000 megawatt coal fired thermal power plant.[23] According to the WHO and the EPA, in the USA, the permissible levels of U in drinking water are 1.4 mgL^{-1} and 30 $\mu\mathrm{gL}^{-1}$, respectively.[24] Moreover, the trace level determination of U(VI) is of prime importance in the nuclear industry due to higher capital cost of uranium metal recovery from its ore and also health related hazards.[25] When analyzing U(VI), it will be advantageous if additional metal ions commonly encountered during analysis, such as Fe(III) and Cu(II) are also accommodated. Moreover, these metal ions are frequently used in acidic or carbonate leaching for oxidation of U(IV).[26] Quality control and quality assurance of purified U(VI) may require assay of the incorporated oxidants. In the current investigation, the IPC method has been investigated by incorporating TAASs of varied lipophilicities with the objective to enhance the resolution of the above mentioned metal ions for improved quantification. In this reference, simulated standards were subjected to analysis for the evaluation of accuracy and precision of the developed method.

EXPERIMENTAL

Chemicals

Tetramethyl ammonium bromide (TMABr), tetraethyl ammonium chloride (TEAC), tetrapropyl ammonium bromide (TPABr), tetrabutyl ammonium perchlorate (TBAP), tetrahexyl ammonium bromide (THAB), tetraheptyl ammonium bromide (THpAB), and tetraoctyl ammonoum bromide (TOABr) were from Fluka, Switzerland. Sodium dihydrogen phosphate and phosphoric acid were from E. Merck, Germany. Standard solutions of 1,000 μg mL^{-1} for each metal ion, in 0.5 M HNO_3, were prepared from analytical grade reagent, (E. Merck, Germany).

Instrumentation

A Perkin-Elmer Series 10 solvent delivery system (USA) was fitted with a 20 μL loop and a Rheodyne 7120 sample injector valve. A variable wavelength UV detector, Kratos 773 (USA), and data processor D-2500, Hitachi, Japan, were used. The reversed phase column was Nucleosil C_{18} from Machery Nagel, Germany. A Pope 1501 pH meter (USA) was calibrated using two standard buffers; mobile phase pH was adjusted with 0.5 M phosphoric acid. All measurements were carried out at room temperature (24 ± 2°C). The mobile phase was prepared as described elsewhere.[4–7]

ANIONIC COMPLEXATION IN PHOSPHATE MEDIA

Uranyl ion complexation with sulphate, phosphate, carbonate, and carboxylate ligands has been reported elsewhere.[26] The nitrato complex of uranium is well known. However, the stronger ligands such as mentioned earlier replaced the nitrato ligand in the uranium complex.[27] The proposed anionic uranium complex $[UO_2\ (H_2PO_4)_3]^-$ has a formation constant $10^{5.3}$.[25,28] This anionic complex has been successfully used for refining of uranium on an anion exchange resin. It is free of cationic interference, particularly of aluminum.[29] The mixed equilibrium constant β is given as follows; its validity has been discussed elsewhere.[5]

$$\beta_{\mathrm{ij}}^{/*} = \frac{[\mathrm{UO_2(i - jH_2PO_4);\ jH_3PO_4}]}{[\mathrm{UO_2}]^{2+\mathrm{a}}\mathrm{H_2PO_4^{i}} \cdot {}^{\mathrm{a}}\mathrm{H^{j}}}$$

The anionic complexation of Fe(III)[30] and a neutral complex of Cu(II) with $H_2PO_4^-$ have been reported.[31] The metal phosphato anionic complex forms an ion-pair, on-column, with a suitable counter cation in a RP-IPC system which is monitored at fixed wavelength in UV region.

RESULTS AND DISCUSSION

RP-IPC with UV detection is a simple, selective, and sensitive technique. IPRs of different lipophilicities were investigated for ion pair formation with negatively charged metal complexes in phosphate media. The effect of the nature and concentration of the IPR, complexing ligand, and the role of the organic modifier and pH have been investigated regarding the retention of metal ion complexes. The regulation of retention behavior of anionic complexes in terms of separation factor α can be generalized according to the following relationship:

$$\alpha = (E_{QX}[Q^+]aq.)^{-1} V_S \cdot V_m^{-1}$$

where (Q^+) refers to the concentration of a counter cation, E_{QX} is extraction constant, and V_s and V_m are phase volume ratios of stationary and mobile phase volume, respectively. Thus, increasing the concentration of the counter ion in the mobile phase causes a decrease of separation factor. The three metal ions Cu(II), Fe(III), and U(VI), were taken to demonstrate the potential role of ion pairing on their retention behaviors on a reversed-phase column. The assay of these metal ions may be required to monitor water quality[24] and to determine the purity of refined uranium.

Influence of Ion-Pairing Reagent on Resolution

The initial mobile phase, consisting of 5 mML^{-1} of TMABr in water with 5 mML^{-1} NaH_2PO_4, at pH 3, resolved only Cu(II), Fe(III), and U(VI) merged with the Fe(III). A variation of 5–90 mML^{-1} of this IPR in the mobile phase did not resolve the Fe(III) and U(VI) pair. Incorporation of 40 mML^{-1} tetraethyl ammonium ion (TEA^+) and 30 mML^{-1} tetrapropyl ammonium ion TPA^+ has improved the R_s of Fe(III)-U(VI) to 0.2 and 0.3, respectively. The addition of moderately lipophilic TBA^+ has significant impact on the separation of Fe and U. It has the advantage of better solubility and prompt equilibration with the RP-column. TBAP separated the three metal ions in 16 minutes, as shown in Fig. 1.

The detection limits and linear ranges of the metal ion with TBAP are reported elsewhere.[5]

Fe(III) and U(VI) were separated, though not to the baseline. The Fe(III)-U(VI) peaks merge if the Fe concentration is ten-fold of the U(VI) concentration. Therefore, in order to improve the Fe(III)-U(VI) separation, the potential role of IPRs having greater lipophilicities was investigated. The presence of THABr, THpABr, and TOABr in the eluent has excellently resolved the three metal ions in approximately 20 minutes. However, the overall analysis time was prolonged, as compared to that of TBA for the investigated IPRs, due to strong retention of nitrate, as shown in Figs. 2 and 3.

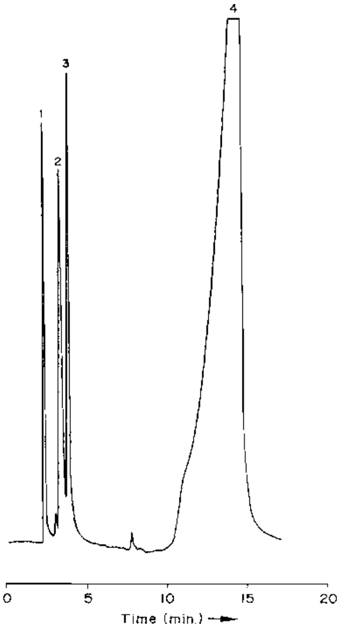

Figure 1. Separation of metal ion mixture. Peaks: 1 = Cu(II) 20 ppm; 2 = Fe(III) 2 ppm; 3 = U(VI) 20 ppm; 4 = NO_3^-, Column = Nucleosil C_{18}, UV = 240 nm; Eluent ACN 3% in H_2O, TBAP = $5 mML^{-1}$, $NaH_2PO_4 = 30 mML^{-1}$, pH = 2, Flow rate = $0.6 mL min^{-1}$.

The influence of lipophilicity in terms of the number of carbon atoms on the separation factor α is given in Fig. 4. The increased lipophilicity of the IPR has a marked effect on α. The separation factor for Cu-Fe is almost double that for $THpA^+$, as compared to TBA^+. It has increased almost five times for the Fe-U separation. All of the metal ions are separated to the baseline. The equilibration of TOAB with the RP-column is slow as compared to IPRs used earlier. The concentration of higher TAASs in the mobile phase has been reduced due to their limited solubilities in organic-aqueous media. The α for Fe(III)-U(VI) indicates that increased lipophilicity of the IPR can accommodate higher concentrations of Fe(III) and minimizes its interference with U. Moreover, other metal ions of interest may be investigated for their analysis. For further investigation, TBA^+ as IPR has been selected to study the influence of various chromatographic parameters.

Effect of Type of Organic Modifier

Various types of organic modifiers are used to avoid risk of turbidity formation or deposition of tetraalkyl ammonium ions and to reduce the irreversible

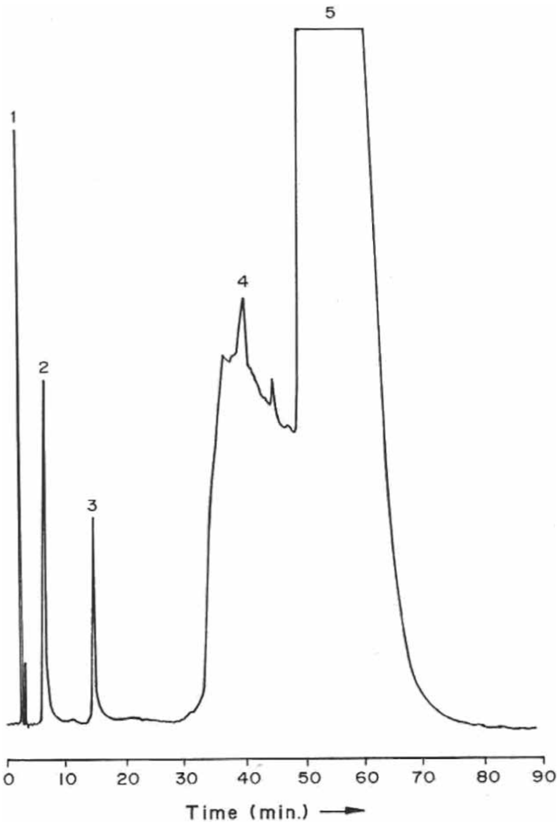

Figure 2. Chromatographic separation of metal ions using 1.5 zmML^{-1}THpABr, MeOH = 40% in H_2O. Peak 4 = Nitrite, 5 = Nitrate. LC condition and peak identification as per Fig. 1.

adsorption of the neutral ion pair. Methanol, acetonitrile, and tetrahydrofuran (THF) were used in the range of 2–20% in the mobile phase. It was observed that individual presence of the above mentioned solvents has no major effect on the elution order of metal ions. However, the sensitivity was affected by changing the solvent, especially at the lowest detection limits (LDL). LDL of all metal ions is nearly constant in methanol and acetonitrile. However, in THF, it is lower when compared with above mentioned solvents, due to its increased background absorbance.

The in situ-formed neutral ion-pairs TAA^+ $[UO_2\ (H_2PO_4)_3]^{-1}$ tend to firmly adsorb onto the surface of a reversed-phase column because of the lipophilic character of the ion-pair. In order to shorten the analysis time, an organic modifier is needed in the eluent to compete with the ion-pair in the adsorption equilbria. The required concentration of organic modifier in the mobile phase depends on the degree of lipophilicity of the incorporated

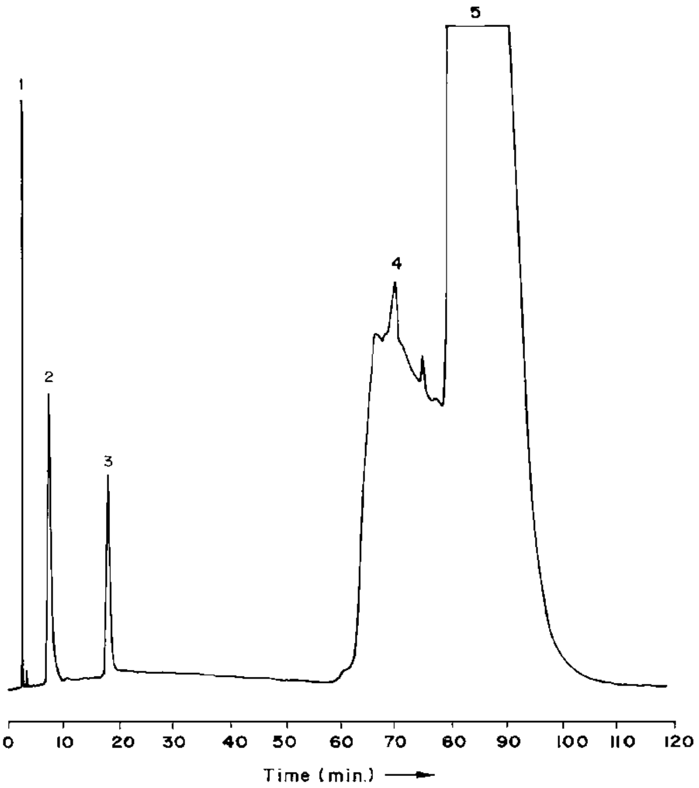

Figure 3. Elution behavior of metal ions in the presence of 1.0 mML^{-1} TOAB, MeOH = 60% in H_2O, experimental condition and peak identification as per Fig. 2.

IPR. Considering the benefits of better resolution and sensitivity of acetonitrile, it was selected for the rest of the studies. The increase in polarity of mobile phase caused by increasing the concentration of ACN results in the decrease in the retentions of the analytes. It may be that higher concentrations of ACN decrease the amount of absorbed TAA^+ ion or rapidly exchange its interaction with column. The concentration effect of acetonitrile on the separation factor (α) is shown in Fig. 5.

Effect of Ligand Concentration

The complexation that takes place between the metal cation and the mobile phase ligand $H_2PO_4^-$ and the concentration of IPR control the retention and resolution of the analytes. The role of HSO_4^- as ligand has been reported elsewhere.[32] In the present study, $H_2PO_4^-$ has been used as a substitute for sulphate to improve performance. A change of 10–50 mML^{-1} NaH_2PO_4

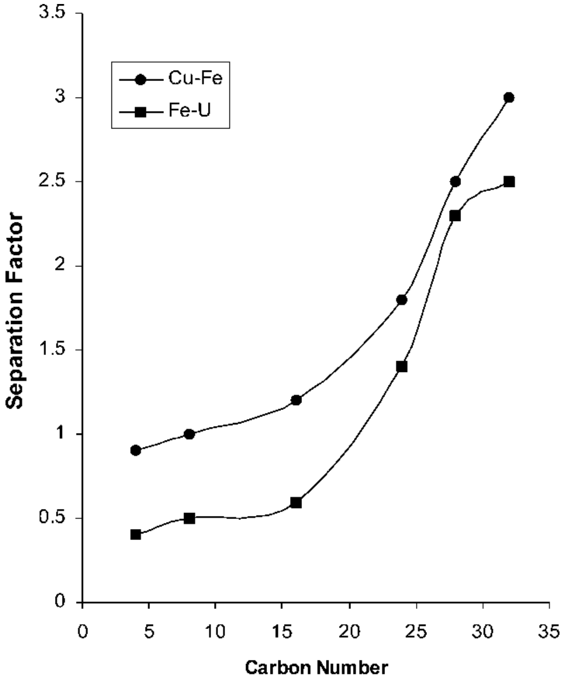

Figure 4. Influence of carbon number (lipophilicity) of the ion pair reagent on the separation factor (α) for Cu-Fe and Fe-U pairs.

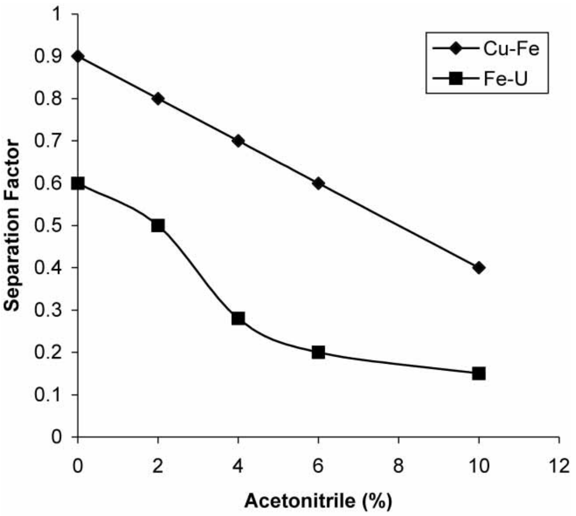

Figure 5. Effect of organic modifier on separation factor for Cu-Fe and Fe-U pairs. Experimental conditions as per Fig. 1 except using ACN.

enhanced the sensitivity for each metal ion, which might be due to an increase in the quantity of phosphato complex formed for the fixed quantity of metal ions injected. Above 50 mML^{-1} NaH_2PO_4, the resolution of ions tends to decrease due to an increase in uncomplexed $H_2PO_4^-$ that might have formed ion-pairs with TAA^+. Hence, interaction of anionic complex with counter ion decreases. For further studies, 30 mML^{-1} NaH_2PO_4 was selected. The impact of $H_2PO_4^-$ concentration on the separation factor (α) is outlined in Fig. 6. It shows that the α value is maximum up to 10 mML^{-1} for Cu(II)-Fe(III) and 30 mML^{-1} for the Fe(III)-U(VI). Thereafter, it exhibited a decreasing trend. This may be due to increased ion-exchange competition of anionic metal complexes and $H_2PO_4^-$ ions with the adsorbed ion-pairing reagent, TAA^+. Considering the optimum separation at 30 mML^{-1} $H_2PO_4^-$, this concentration was used for further investigation. The incorporation of $H_2PO_4^-$ instead of hydrogen sulphate medium has a number of advantages. These include improved lowest detection limit of 2 ppm as compared to 20 ppm for U(VI), disappearance of an acidic peak which appears at pH 3 and interferes with the Fe(III) peak, and enhanced tolerance of sample acidity up to 0.5 M HNO_3 as compared to 0.3 M HNO_3 with HSO_4^-.[32]

Influence of pH

In the determination of anionic metal complexe ions, the retention behavior can be influenced by mobile phase pH. However, it should be adjusted carefully, as it will affect the stability of the metal-ligand complexes and, with a higher pH, there is a risk of metal hydroxide complex formation.[33] A variation in mobile phase pH may help in improving separation factor and sensitivity. It was varied from 3 to 2 in steps. A gradual increase in the sensitivity of all the metal ions was observed by lowering the pH, while keeping the concentration of ion-pair reagent and buffer ligand constant. The pH of the eluent influences the course of complex formation.[34] A pH

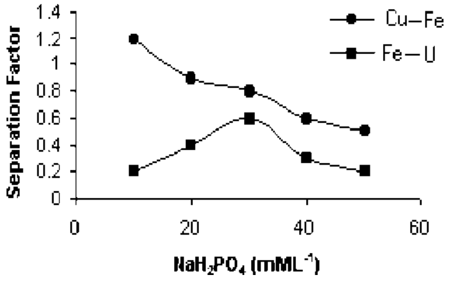

Figure 6. Effect of ligand concentration on separation factor for Cu-Fe and Fe-U pairs. Experimental conditions as per Fig. 1 except using $H_2PO_4^-$.

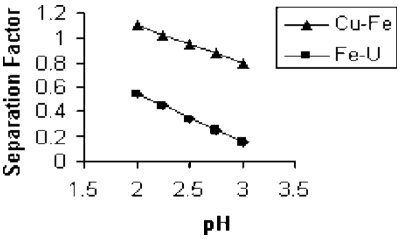

Figure 7. The pH influence on separation factor for Cu-Fe and Fe-U pairs. Experimental conditions as per Fig. 1 except for the pH.

of 2 has the advantages that the acidity peak which interfered with iron at pH 3 was merged into the baseline and sensitivity of all metal ions is remarkably increased. The lower sensitivity at pH 3 may be probably due to formation of hydroxy metal complexes or because of a decrease in the concentration of metal phosphato complex.[33] The effect of pH on separation factor (α) is shown in Fig. 7. The decreasing trend of separation factor may be due to the lower retention of anionic metal complex at high pH.[34] It may lead to the association of counter ion with OH^- ion and, hence, reduction of the separation factor for metal complex.

Influence of Diverse Ions

The potential interference from a variety of elements has been investigated. The selected metals and anions are listed in Table 1. The concentrations of selected elements was the same as those which are usually found in real samples; elements were injected individually under the optimized experimental condition. It was found that none of the investigated ion interfered significantly. Simulated synthetic mixtures of three metal ions of variable concentrations were analyzed to observe the concentration effect on elution behavior. These were also analyzed by AAS for copper and iron, whereas inductively coupled plasma-optical emission spectroscopy was used for uranium. The emission line selected for uranium was 385.958 nm and the analysis was carried out using matrix matching standard. The results are

Table 1. Tolerance limits for various expected interfering ions (mgL^{-1})

Elements	Concentration
Na, K, Mg, Sr, Ba	150
Al, Mn, Ni, Mo	40
Zr, La, Pr, Nd, Gd, Th, F, Cl, Br, SO_4	30

Table 2. Performance comparison of IPC with the AAS/ICP-OES for the analysis of metal ions (mgL^{-1})

	Known Concentration			IPC			AAS/ICP-OES[b]		
Sample[a]	Cu(II)	Fe(II)	U(VI)	Cu(II)	Fe(II)	U(VI)	Cu(II)	Fe(II)	U(VI)[b]
S1	5	40	5	5.1 ± 0.2	39 ± 2	4.8 ± 0.2	5.1 ± 0.1	39 ± 1	4.8 ± 0.4
S2	60	20	60	59.4 ± 0.5	19 ± 0.8	59 ± 2	61 ± 2	21 ± 0.2	61 ± 0.1
S3	60	500	5	59.4 ± 0.5	504 ± 5	4.6 ± 0.4	60.5 ± 0.4	510 ± 5	5.5 ± 0.2

[a] Simulated synthetic mixture of metal ions.

[b] Uranium analyzed using ICP-OES.

compared in Table 2. For samples where the Fe concentration exceeds ten-fold of the concentration of U(VI), a masking agent, DTPA, was used to overcome the interference of Fe(III) and, later, was determined in an independent run by appropriate dilution. The results show that recovered concentrations of the simulated standards are in agreement when compared with counter techniques.

Performance Comparison of Ion-Pairing Reagents

This study of variety of IPRs revealed that the increase in organic chain length provides better separation of the investigated metal ions. The use of TBA^+ ion partially resolved the Fe(III) and U(VI) peaks. Even a slight increase in the concentration of Fe(III) merges these two peaks. The problem of Fe(III) interference was earlier solved by masking it with EDTA and DPTA. However, the use of higher chain IPRs has led to separation of Fe(III) from U(VI), having a separation factor of five-fold and 6.5-fold with THpBr and TOABr, respectively, as compared with TBA^+; it also avoids the use of a masking agent. Moreover, the improved separation of the three metal ions also provides an opportunity to accommodate additional metal ions for further investigation. The removal of nitrate, due to its longer retention, is under investigation by using columns in series. The three metals have been separated from bulk nitrate within 3–4 minutes on the cartridge column. It is intended to analyse these early separated metal ions free of nitrate on an analytical column to optimize the analysis time. Further work in this direction is underway.

CONCLUSION

The present method is capable of simultaneously analyzing the three metal ions Cu(II), Fe(III), and U(VI). It is relatively simple, sensitive, selective, and fast. In the present chromatographic analysis, uranium is eluted last and interferes least if present in bulk quantity. Therefore, the reported method could be used for analyzing traces of Fe(III) and Cu(II) as impurities in “pure” uranium. Additionally, the developed method may be incorporated to detect toxic metals like Cu and U after appropriate preconcentration in order to comply with various drinking water guidelines.

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