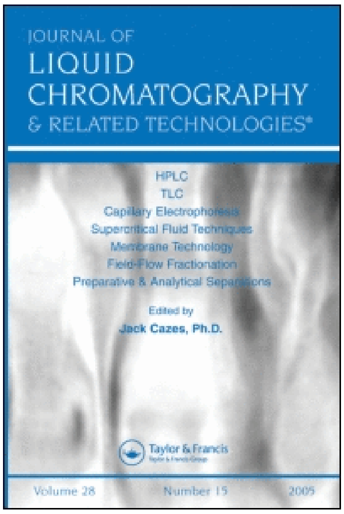

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Abstract: Various masking agents such as ethylenediamine tetra-acetic acid (EDTA), diethylenetriamine penta-acetic acid (DTPA), ethyleneglycol-2-(amino-ethyl) tetra-acetic-acid (EGTA), ascorbic acid, fluoride, tartrate, citrate, oxalate, thiourea, triethanolamine (TEA), and ethylenediamine (EDA) have been used in the sample processing to eliminate the iron interference in the determination of uranium U (VI) by ion-pair high performance liquid chromatography (IP-HPLC). Among the investigated masking agents, oxalate, thiourea, TEA, EDA interfere. However, EDTA and DTPA, are effective to mask iron without affecting U (VI) quantification, while citrate slightly reduces the response. The lowest detection limits for the reported method in standard solution is 2 ppm. The developed method has been applied to analyze U (VI) in simulated standards and IAEA SRM, such as Torbernite ore containing iron. The relative standard deviation (RSD) for uranium determination in Torbernite ore ($n = 5$) is $\sim$2%.

Keywords: Demasking, Torbernite ore, Ion pair HPLC (IP-HPLC)

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INTRODUCTION

The trace level determination of uranium in natural, underground, or waste water is of great environmental concern.[1] Assay of uranium in its more stable hexavalent state is often preferred because U (IV) is unstable and easily oxidized by atmospheric oxygen, even in the presence of protective reagents such as ascorbic acid.[2] Uranium quantification in the presence of different mineral impurities is a difficult analytical task, especially as the uranium contents being determined are much smaller than the level of impurities. Trace amounts of various metals such as zirconium, hafnium, thorium, iron (III), and rare earth elements, when present above certain concentration, interfere in U (VI) analysis and require their prior separation.[3] Matrix removal requires a solvent extraction step, and has various associated problems in terms of reproducibility, simplicity, selectivity, and sensitivity.[1] Separation of interferents by an ion-exchanger is often time consuming and tedious. The traces of organic compounds from ion exchange resins must be removed for accurate analysis.[4] In ICP-AES analysis of extracted uranium, an increase in background intensity or plasma quenching due to the presence of organic solvent are observed on direct introduction of the organic extract into the plasma.[5]

Aminopolycarboxylic acids (EDTA, NTA, DTPA, EGTA) are useful for the masking of multivalent metals in neutral and alkaline media. In the photometric determination of U (VI) using Arsenazo (III), the presence of complexing agents EDTA, 1,2-diamino cyclohexane tetra acetate (DCTA) considerably reduces the sensitivity of U (VI).[6] Furthermore, the photometric method requires critical control of pH, and precipitation of complexans (EDTA, DCTA) at pH 1–2 incorporate various complications.[7] In the separation and preconcentration of uranium in the presence of iron and copper, EDTA has been used as a masking agent employing solid phase extraction (SPE), and the separated uranium was assayed using a differential pulse polarography technique.[8] Alkaline earth metals were successfully determined in high iron containing matrix-using EDTA by ion-chromatography.[9] Chromium ion speciation has been reported using EDTA and DCTA in the sample using IP-HPLC.[10,11] Various cations and anions were resolved using IPC by incorporating complexing agents such as NTA, DTPA, and EGTA, etc. in the eluent.[12] U (VI) is routinely analyzed in ores and minerals and it is observed that high contents of iron interfere with uranium quantification in IP-HPLC. The interference has been overcome by incorporating EDTA as a masking agent in the sample solution.[13–15] Ascorbic acid, fluoride, tartrate, citrate, DTPA, oxalate, thiourea, TEA, and EDA are frequently used to mask Fe (III) in various analytical procedures.[16] In the present investigation, the masking potential of these complexans has been explored to analyze uranium in iron containing matrix to minimize the iron interference using IP-HPLC.

EXPERIMENTAL

Reagents and Materials

Tetrabutylammonium perchlorate (TBAP) was from Fisher scientific company, USA. Uranyl nitrate, ferric sulphate, NaH_2PO_4, H_3PO_4, HNO_3, sodium citrate, sodium oxalate, sodium fluoride, ascorbic acid, all of analytical grade, and acetonitrile, Lichrosolv grade, were from E-Merck, Germany. DTPA, EGTA, EDTA, EDA, were from Fluka, Switzerland. Thiourea was from May and Baker LTD, Dagenham, England. Triethanolamine was from Riedel de haen seelze, Hannover, Germany. The masking agents were dissolved in deionised water, except EDTA, EGTA, and DTPA, which were dissolved in deionised water along with small quantity of one Molar NaOH to make the solution clear.

Instrumentation

Solvent delivery system series10 Perkin Elmer, USA was fitted with a 6 μL loop and Rheodyne 7120 sample injector. A UV-VIS detector Kratos, 773, USA was used. Printer/plotter D-2500, Hitachi, Japan was used for recording chromatograms. The analytical column was Euro sphere C_{18} (250 × 4.6 mm) from Knauer, Germany. pH meter Pope 1501, USA was calibrated with two standard buffers and mobile phase pH was adjusted with 0.5 M phosphoric acid. A microwave digester MW 500, Arura, Canada was used for ore dissolution.

Dissolution of Samples

The standard reference material (SRM) Torbernite with known uranium concentration was obtained from IAEA, Vieana. The solutions of these samples were prepared using microwave assisted dissolution by modifying the EPA standard procedure 3052. To a 0.563 g SRM, 4 mL aquea regia and 2 mL HF were added and subjected to microwave digestion for 15 minutes at 180°C. After cooling, 1 mL concentrated $HClO_4$ was added and contents were heated to fuming. Another 3 mL of aquea regia and 1 mL concentrated $HClO_4$ were added and fumed to semi-dryness. These contents were finally made up to 50 mL 0.5 M $HNO_{3.}$ The acidity of the sample was varied as per requirements for further investigation.

RESULTS AND DISCUSSION

Ion-Pair Chromatography Using Metal Phosphato Complex

Uranyl, iron, and copper ions complexation with dihydrogen phosphate ligand in acidic media has been used to develop an IP-HPLC method for the respective metals. The $H_2PO_4^-$ ligand can easily replace weaker ligands and form anionic complex $[UO_2\ (H_2PO_4)\ _3]^-$ having formation constant $10^{5.3}$.[17,18] The mixed equilibrium constant β is given as follows, and its validity has been discussed elsewhere:[14,20,21]

$$\beta_{ij}^{/*} = [UO_2(i - j\ H_2PO_4);\quad jH_3PO_4]/[[UO_2]^{2+a}H_2PO^{i}_{4.}{}^{a}H^{j}]$$

The metal phosphato anion complex forms an on-column ion pair with a suitable counter cation such as tetrabutyl ammonium (TBA^+) in IPC separation. The elution behaviour of U (VI) in IPC is shown in Fig. 1. However, iron is mostly associated in ores containing tracer uranium and causes interference during uranyl analysis. It has been observed that iron strongly

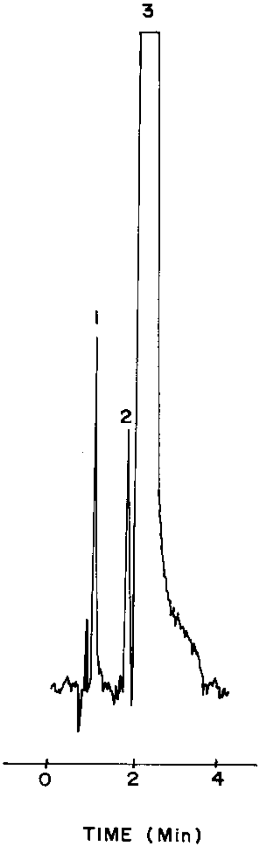

Figure 1. Elution trend of standard U (VI) metal ion in 0.1 M HNO_3. Column: Knauer Eurosphere C_{18} (250 × 4.6 mm), Eluent composition: Acetonitrile: 3% in H_2O, TBAP 5 mM, NaH_2PO_4: 30 mM, pH; 2, Flow rate 1.5 mL min^{-1}, UV = 240 nm, FS 64 mV, Peak identification: 1 = U (VI), 100 ppm, 2 = NO_2^-, 3 = NO_3.

interferes with U (VI) analysis in IPC and it masks uranium peak as shown in Fig. 2.

Masking of Iron by Complexans

Complexing agents such as DTPA, EGTA, EDA, and TEA are used for eliminating iron interference during metals analysis.[16] In the present investigation, effectiveness of these agents to overcome iron interference has been compared with EDTA regarding uranyl analysis. The role of the individual complexing agent was evaluated in the concentration range of 10–100 mM for a fixed concentration of 1000 and 100 ppm of iron and uranium, respectively. The complexing agents EDA, TEA, and EGTA were precipitated

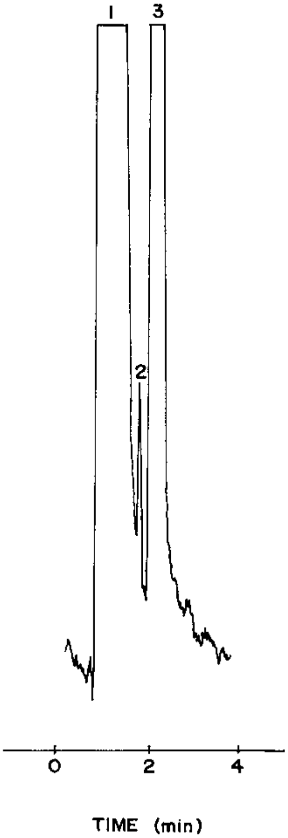

Figure 2. Masking of U (VI) by Fe (III) in standard metal mixture. Chromatographic conditions are as per Fig. 1. Peak identification: 1 = Fe (III) 1000 ppm + U (VI), 100 ppm, 2 = NO_2^-, 3 = NO_3^-.

with standard uranium metal solution in 0.1 M HNO_3. The other tested agents, tartrate, thiourea, and ascorbic acid co-elute with uranium. Although oxalate demasked iron, it also drastically reduced the sensitivity of uranium.

The Role of DTPA

The concentration of DTPA was varied to demask the effect of tenfold iron in uranium standard solution. The variation of separation factor α for the U (VI)-Fe (III) pair, for varied concentrations of DTPA, is depicted in Fig. 3 and is compared with EDTA. It reflects that DTPA demasks iron at higher concentration as compared to EDTA, and so it is a weaker demasking agent. The demasking effect of DTPA is depicted in Fig. 4. The elution behavior shows no prominent effect on the signal height of U (VI), its baseline and retention time. The U (VI) peak in a simulated standard containing iron was also confirmed by the standard addition method.

The Influence of Oxalate and Citrate

The addition of 40 mM oxalate drastically reduced the signal intensity of 1000 ppm iron and 100 ppm uranium to almost baseline, as is indicated in

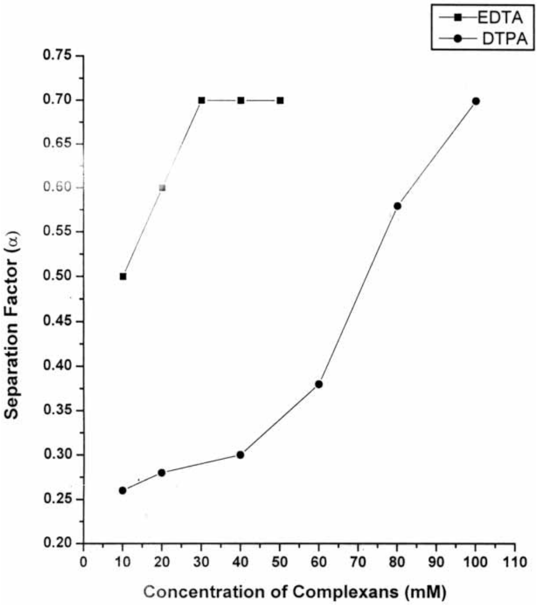

Figure 3. Variation of α for U (VI)-Fe (III) pair for varied concentrations of EDTA and DTPA in demasking iron for uranium quantification. Fe (III) 1000 ppm, U (VI) 100 ppm, Chromatographic conditions are as per Fig. 1.

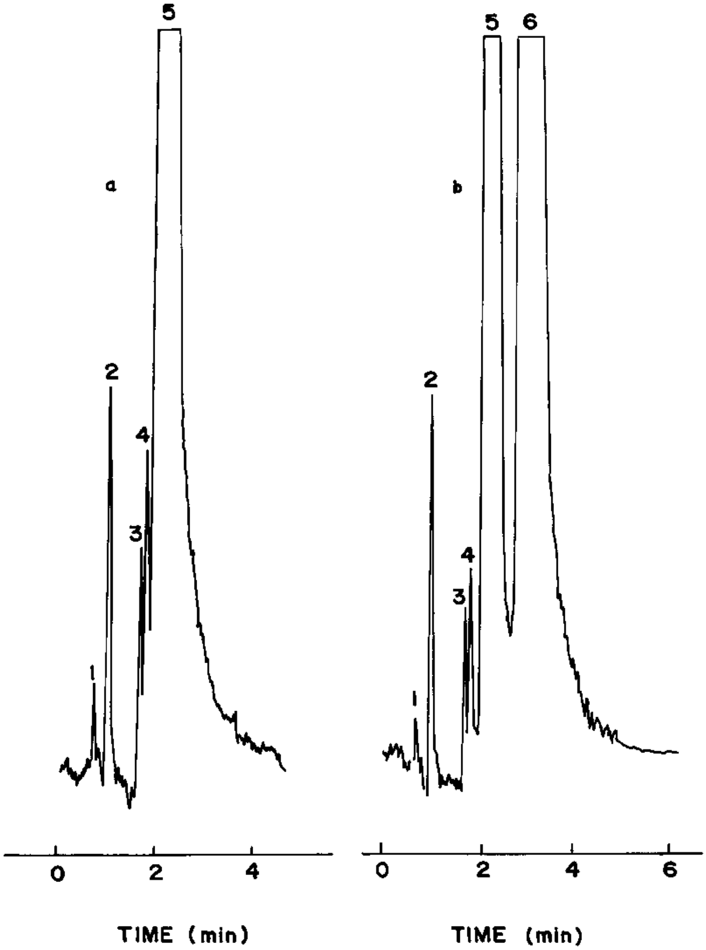

Figure 4. (a) Demasking of 1000 ppm Fe (III) by 20 mM EDTA containing 100 ppm U (VI), LC conditions are as per Fig. 1, Peak identification 1 = Cu (II), 2 = U (VI) 100 ppm, 3 = Unknown, 4 = NO_2^-, 5 = NO_3. (b) Demasking of 1000 ppm Fe (III) by 100 mM DTPA: Peak identification 1 = Cu (II), 2 = U (VI) 100 ppm, 3 = Unknown, 4 = NO_2^-, 5 = DPTA, 6 = NO_3^-.

Fig. 5. This was revealed during U (VI) analysis using IPC; care must be taken that oxalate is not incorporated at any stage. The use of citrate did mask the presence of iron. However, it slightly reduced the signal intensity of U (VI) as compared to the use of EDTA and DTPA. In addition to this, a drift in baseline and slight deterioration of Fe-U resolution is also observed as shown in Fig. 6. Considering the advantage of DTPA, further investigation for oxalate and citrate is discontinued.

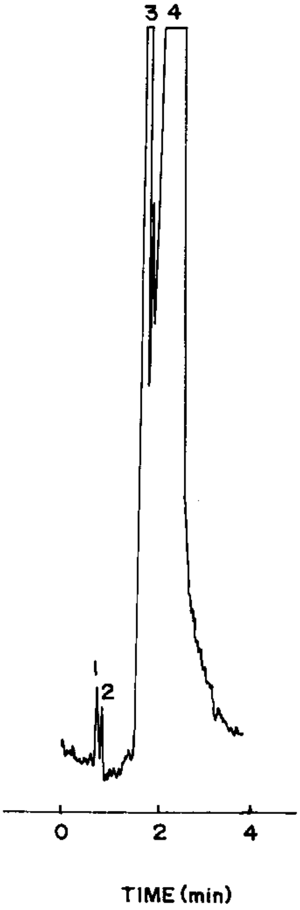

Figure 5. Masking effect of oxalate on the metal ion analysis. 100 ppm uranium completely masked, Peak identification: 1 = Cu (II), 2 = Fe (III) 1000 ppm, 3 = Oxalate 40 mM, 4 = NO_3^-. LC conditions are as per Fig. 1.

Effect of Sample Acidity

Sample acidity affects demasking efficiency of a masking agent. In this context, acidity was varied from 0.1 to 0.9 M HNO_3. It was observed that EDTA exhibited a good demasking effect up to 0.4 M and U (VI) recovery was ~98%; thereafter, it starts precipitation. The acidity tolerance capacity of DTPA is better and was not precipitated even at 0.9 M HNO_3, and U (VI) recovery is not affected. The details are summarized in Table 1. We have concluded that EDTA seems to be the better complexing agent for effective demasking of 1000 ppm iron at moderate pH, while DTPA has an

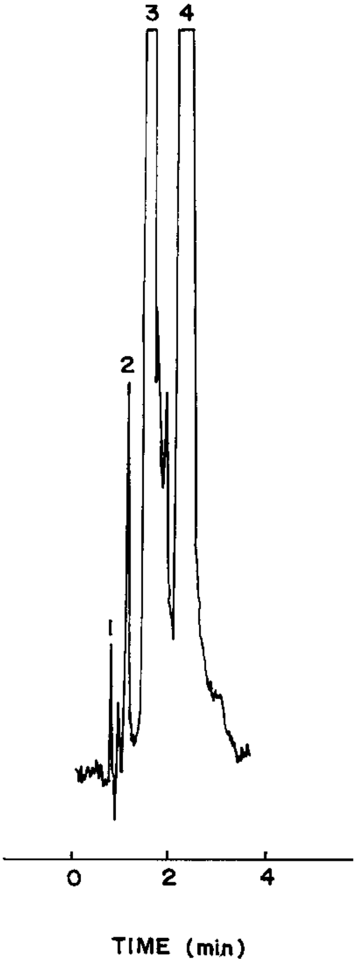

Figure 6. Demasking of 1000 ppm Fe (III) by citrate, Peak identification: 1 = Cu (II), 2 = U (VI) 100 ppm, 3 = Citrate, 4 = NO_3^-. LC conditions are as per Fig. 1.

edge at lower pH as shown in Table 1. It is particularly advantageous for uranium ore and coal ash analysis containing high concentration of interferents like iron, where relatively high sample acidity is preferred to keep the analyte of interest and interferents in solution.

The overall formation constant for Fe (III)-DTPA complex is 28.6. This may be compared with 25.2 for the EDTA complex.[19] In addition, pK_3 for the acid dissociation of DTPA is considerably lower than pk_3 for EDTA. This will favour complexing action at low pH. Furthermore, probably because of the lower value of its pk_1 (1.7) of DTPA, it is considerably more

Table 1. Effect of acidity on (%) recovery of uranium from a mixture[a] of iron and U (VI)

Acidity[b]	EDTA[c]	DTPA[d]
0.1	99.5	98.8
0.2	99.0	98.5
0.3	98.2	98.7
0.4	98.2	98.4
0.5	Precipitation (Ppt)	98.7
0.6	PPt	98.5
0.7	PPt	98.5
0.8	PPt	98.2
0.9	PPt	97.4

[a] Fe (III) 1000 ppm, U (VI) 100 ppm.
[b] Molar concentration.
[c] 20 mM.
[d] 100 mM.

stable in acid solution than EDTA. It therefore seems to be advantageous for demasking Fe (III) in acid solution for U (VI) determination.

Analysis of Standard Reference Material

The optimized IPC method for the analysis of a synthetic simulated mixture of uranium and iron was evaluated to analyze real uranium bearing ore. The Torbernite ore is a standard reference material of IAEA, containing 0.471% U_3O_8. Its iron content measured by AAS was ~97 ppm. It was dissolved as described earlier. The main objective of this analysis was to check the influence of high acidity on the recovery of uranium in real samples, and to determine if there is advantage over the use of EDTA. The elution pattern of uranium in the Torbernite ore is described in Fig. 7. The presence of uranium is also confirmed by the standard addition method. The Uranium concentration in Torbernite found by the present method is 44 ± 2 ppm, whereas the certified value is 45 ppm. This concludes that the incorporation of DTPA as a demasking agent has a positive impact for the assay of uranium. The uranium content in Torbernite, was also determined by the Br-PADAP photometric method;[22] it was 46 ± 3 ppm, which is in close agreement with the reported method.

CONCLUSION

Incorporation of complexing agents to over come interference is a relatively simple and selective approach as compared to the use of liquid/liquid extraction, ion- exchange, and other methods. The advantage of the reported

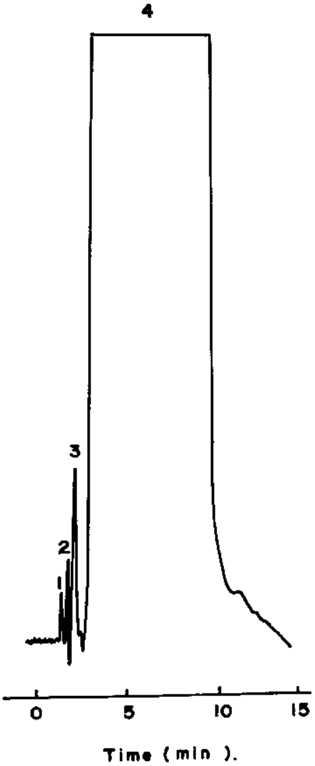

Figure 7. Demasking of iron by DTPA for the analysis of U (V) in SRM Torbernite, LC conditions as per Fig. 1. Peak identification: 1 = Unknown, 2 = Iron, 3 = Uranium, 4 = Nitrate 0.5 M.

procedure over the extractive photometric methods is its simplicity and quantitative separation of U (VI) from interfering iron. The use of DTPA is more attractive to suppress iron interference in a more acidic solution. The EDTA and citrate are more effective in mild acidity. The rest of the complexing agents either co-elute with the uranium or are ineffective in suppressing iron. Further work is in progress to optimize the incorporation of citrate regarding analysis of uranium in different matrices.

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