Flow Injection Spectrophotometric Determination of Uranium With In-valve Ion-exchange Column Preconcentration and Separation

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An in-valve column containing Duolite C-225(H) resin for preconcentration and separation flow injection determination of uranium is described. Uranyl ions loaded on the column were eluted with 1 mol l^{-1} HCl and mixed with a stream of buffer and masking solution [triethanolamine (1 mol l^{-1}) and 1,2-cyclohexanediaminetetraacetic acid (0.7% m/v)]. After passing through a glass bead column the complex product was continuously monitored at 530 nm. Calibration by time (or volume) using a single standard was performed up to 7 µg of U. The detection limit (3σ) and relative standard deviation were 0.27 µg of U and 2.1% (for 2 µg; $n = 12$), respectively. Interferences of some ions were studied. Applications to the determination of uranium in rock and water samples are described.

Keywords: *In-valve ion-exchange column; preconcentration; separation; flow-injection; uranium; Duolite C-225(H); spectrophotometry; 4-(2-pyridylazo)resorcinol*

Introduction

Several analytical techniques have been proposed for uranium determination in various matrices. For example, Decambox *et al.*[1] developed a laser-induced time-resolved spectrofluorimetric method for trace uranium determination in human urine. Franek *et al.*[2] described a radiochemical NAA technique for the determination of sub-nanogram per gram concentrations of thorium and uranium in various high-purity microelectronic materials. Results obtained compared favourably with those obtained by INAA and ICP-MS. Das *et al.*[3] demonstrated a differential-pulse polarographic (DDP) method for the determination of uranium(vi) in the presence of a large excess of thorium. Nashine *et al.*[4] devised a simple selective and sensitive spectrophotometric method for determining uranium in geological samples. It is based on the reaction of U^{IV} with thorin and subsequent extraction of the red–orange complex into *N*-hydroxy-*N,N'*-diphenylbenzamidine followed by spectrophotometric measurement at 390 nm. Recently, ICP-MS has been reported as a highly sensitive means for analysing uranium in real samples.[5,6] In the case of real sample analyses, the sample pre-treatment procedures are tedious. The problem can be overcome by using an on-line flow injection (FI) system for preconcentration and separation of the analyte.[7,8]

Ion-exchange preconcentration has proven to be an effective means of increasing the sensitivity of an analytical determination and also a means of removing interferences.[9]

Batch ion-exchange preconcentration can increase the sensitivity of procedures but uses large sample volumes, has a low sample throughput and is slow.[10]

There has been interest in on-line preconcentration since 1980[9,10] and many modifications have been proposed to improve its performance.[11] This approach not only increases the speed of the concentration process, but also enhances the selectivity, sensitivity, detection limit and sample throughput.

Incorporating ion exchange with FI offers additional advantages in situations where on-line pre-treatment of the sample involves separation and preconcentration.[12–17] Although the first on-line column applied for FI was one for use with a UV/VIS spectrophotometer as detector,[10] such development has centred mainly on AAS.[13] Flow injection methods have been developed for determination of trace uranium levels in geological samples, but are not sufficiently free from interferences for application to certain other samples.[15,16] Pavon *et al.*[7] performed a detailed study of on-line ion-exchange preconcentration with a microcolumn for uranium determination in water samples but so far the in-valve microcolumn has not been used for the FI determination of uranium.

This paper describes the preconcentration of uranium on Duolite C-225(H) resin packed in a dual column of sample loops in the injection valve and subsequent FI. The reaction is between U^{IV} and 4-(2-pyridylazo)resorcinol (PAR) in triethanolamine buffer solution pH 8.0. This reaction has been previously reported for batch spectrophotometry.[18,19] The method is cost-effective, selective, sensitive and precise. Applications to rock and water samples are proposed.

Experimental

Reagents

All chemicals were analytical-reagent grade and de-ionized water was used. The standard stock uranium solution of 1000 µg l^{-1} was prepared by dissolving uranyl nitrate hexahydrate (2.1095 g, obtained from Merck, Darmstadt, Germany) in 1 l of water. Further dilutions with water were made for appropriate concentrations. The colour reagent was 0.02 g of PAR (Sigma, St. Louis, MO, USA) dissolved in 100 ml of 0.1 mol l^{-1} sodium hydroxide. The eluent solution was 1.0 mol l^{-1} hydrochloric acid. The buffer–masking solution was prepared by dissolving 135 ml of triethanolamine and 7.0 g of 1,2-cyclohexanediaminetetraaceticacid (CDTA, obtained from Fluka, Bachs, Switzerland) in 500 ml of water, adjusting the pH to 10 with 10% m/v sodium hydroxide solution and diluting to 1 l with water. Duolite C-225(H) resin, 14–30 mesh

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USS (Rohm and Haas Philadelphia, PA, USA) was soaked overnight in 6 mol l^{-1} HCl before washing and rinsing with water.

Apparatus

The in-valve micro ion-exchange column

A pre-treated portion of Duolite C-225(H) resin (0.30 g) was packed into silicone tubing (3.2 mm id, 6 cm): the two ends of which were then closed with Teflon wool plugs covered with plastic adapters connected to Teflon tubing of the sample loop size (0.82 mm od) for inserting into the injection valve rotor. Two of these columns replaced sample loops of the injection valve previously described.[20]

The column can be regenerated by passing 6 mol l^{-1} hydrochloric acid solution for 1 min followed by water for 2 min at a flow rate of 4.0 ml min^{-1}.

Flow manifold

The manifold used is shown in Fig. 1. An Eppendorf EVA peristaltic pump (Flaton, USA) was used for propelling the PAR solution (C), the buffer–masking agent solution (B) and the hydrochloric acid eluent (E). The stream line was connected to one of two in-valve micro ion-exchange columns (MC) positioned in the injection valve as described above. The uranium sorbed on the resin in the column was then desorbed by eluent. At the same time uranium was loaded onto the other in-valve microcolumn by passing a standard or sample solution through by means of a suction system using an aquarium pump (AQ).[20] The columns were washed (De) or regenerated (Re) similarly; three-way stopcocks (TWS; Conecta, Sweden) were used to control directions for these lines.

The eluent containing uranium flowing from the injection valve was mixed with buffer–masking stream before merging with the colouring solution. The merged streams were passed through a mixing device (MD) consisting of a single string of glass beads (3.0 mm diameter) in a column of silicone tubing 3.2 mm id 10 cm long.[21] The coloured product was passed through a flow cell (Hellma, 1 cm, Suprasil I window) in a spectrophotometer (Ismatec, green LED for 530 nm) connected to a recorder (Philips PM 8251) for continuous monitoring. All connecting tubes were of Teflon (0.8 mm id).
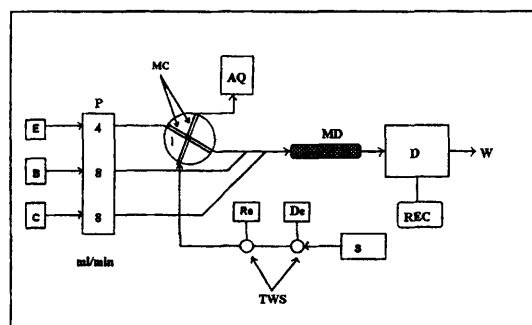

Fig. 1 FI manifold. E, eluent (HCl); B, buffer–masking solution (triethanolamine–CDTA); P, peristaltic pump; C, colouring reagent (PAR); MC, micro-ion exchange column; I, injection valve with two loops; Re, regeneration solution (HCl); De, de-ionized water; S, sample solution; TWS, three-way stopcock; AQ, suction system using an aquarium pump;[21] MD, mixing device (glass bead column);[22] D, spectrophotometer; REC, recorder; W, waste.

Procedure

Construct a standard curve by passing a single standard solution through the in-valve microcolumn at a constant flow rate (1.0–4.0 ml min^{-1}) for various time intervals (1–40 min) depending on the concentration of U^{VI} in the sample solutions. Wash the column with water for 1 min. Elute the column and merge the eluent stream with buffer, masking agent and PAR before detection. Plot a graph of peak height *versus* amount of U. Treat sample solutions similarly and interpolate their responses on the curve.

Application to Rock and Water Samples

Rock

Weigh 0.5–1.0 g of the samples (less than 200 mesh, USS, dried at 110 °C) into a Teflon beaker, moisten with water and add 10 ml of 27.8 mol l^{-1} hydrofluoric acid and 10 ml of 14.6 mol l^{-1} nitric acid. Allow to pre-digest for 1 h on a steam bath and to evaporate to complete dryness. Add a further 5 ml of 14.6 mol l^{-1} nitric acid and again evaporate to dryness. Add 20 ml of 4.0 mol l^{-1} nitric acid and warm again on the steam bath to dissolve all soluble matter. Filter the solution. Adjust the pH of the filtrate to 3–5 with 10% m/v sodium hydroxide solution before diluting with water to 200.0 ml. Store the diluted solution in a plastic bottle.[22]

Water

Water samples should be collected and stored in plastic bottles with addition of 14.6 mol l^{-1} nitric acid (5 ml of acid per litre of water).[23] Samples are filtered, pH-adjusted, and diluted, as described above for rock samples.

Results and Discussion

Optimization of the Manifold

The parameters kept constant were: elution with 1 mol l^{-1} hydrochloric acid at flow rate of 4.0 ml min^{-1}; concentration of triethanolamine buffer 1 mol l^{-1}; masking agent, 0.7% m/v CDTA; and reagent solution, 0.02% m/v PAR in 0.1 mol l^{-1} NaOH. The effect of the concentration of hydrochloric acid, shown in Fig. 2, indicates that a high recovery of uranium 96.4% and a stable baseline can be obtained. When the concentration of hydrochloric acid is higher than 1.0 mol l^{-1}, the mixed solutions become warm and air bubbles may be observed, resulting in low peak heights, noisy peaks and baseline. Hence, the sensitivity and reproducibility deteriorate. Noise might be due to the Schlieren effect and pH gradients.[13] When the concentration of hydrochloric acid is lower than 1.0 mol l^{-1}, recoveries are low due to hydrolysis of uranium.
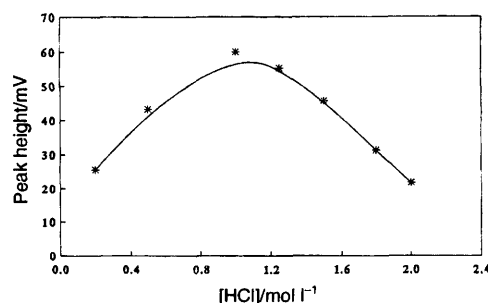

Fig. 2 Effect of eluent (HCl) concentration on the elution of U^{VI} from the Duolite C-225 (H) microcolumn.

When the concentration of the buffer solution was varied from 0.25 to 1.25 mol l⁻¹ triethanolamine the pH value of the final solution remained between 7.9 and 8.2, the optimum range for colour development of the U^{VI}–PAR complex. A concentration of 1.0 mol l⁻¹ triethanolamine was therefore selected.

Duolite C-225(H), Dowex 50W-X8(H) and Amberlite IR 120(H) were examined for the preconcentration of small amounts of U^{VI} in the rock extracts and for water samples spiked with 10 µg ml⁻¹ of standard U^{VI}. The mean recoveries were 96.93, 86.81 and 91.92% for Duolite, Dowex and Amberlite, respectively. Duolite was finally chosen for further investigation due to its high capacity (2.0 mequiv ml⁻¹ of resin bed). Columns of 3, 4, 5, 6, and 7 cm in length with 0.3 cm id were tested. The highest peaks and lowest blanks were recorded using a 5 cm length column (Fig. 3). Fig. 4 shows the effect of flow rate on preconcentration.

Peak heights are unchanged for loading flow rates in the range 1.0–4.0 ml min⁻¹, but decrease at higher flow rate. Effect of flow rate on elution was studied by adjusting the pump speed. Eluent flow rates of 1.5, 2.5, 4.0, 7.2, 9.3 and 12.0 ml min⁻¹ corresponded to the flow rate of buffer and the colouring streams of 4, 6, 8, 10, 12 and 14 ml min⁻¹: resulting in respective peak heights of 35.2, 52.8, 77.2, 61.6, 53.6 and 47.2 mV. At a flow rate of 4.0 ml min⁻¹ elution is quantitative within 8 s and the dispersion is low. Slower flow rates cause higher dispersion. At high flow rates, leakage of solution at the column occurs.[15] These factors govern the possible range of flow rates and the sensitivity and sampling frequency of the method. With the dual columns operated alternately for 2 min each for loading and elution, a sampling frequency of 20–25 h⁻¹ was achieved. For a very low concentration solution, a longer loading time will be required, such as a 1.8 microlitres of uranium per litre of solution by loading for 40 min with a flow rate of 4 ml min⁻¹, *i.e.*, 160 ml of the sample will be used for preconcentration.
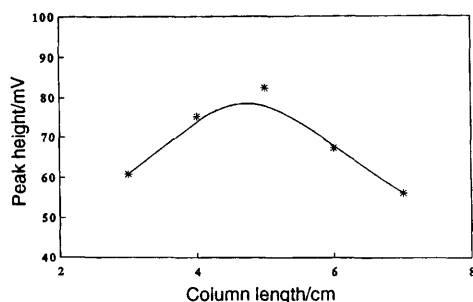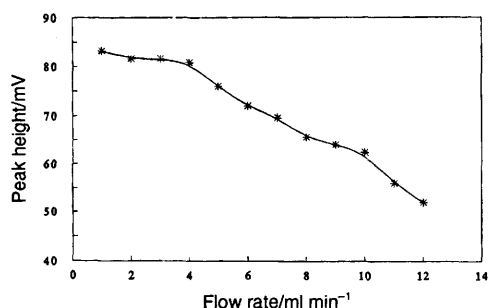
Effect of Sample pH on Preconcentration of Uranium

Important variables affecting the separation of cations on ion-exchangers are the pH of solution and the presence of other cations in the sample solution.[18] The influence of the pH of sample solution on peak height was studied using a standard (1 µg ml⁻¹) adjusted to pH from 1 to 8. Results shown in Fig. 5 indicate that there is no pH effect in the range 2–8.

Interference Studies

Following the recommended procedure solutions containing 1 µg ml⁻¹ U and the respective ion with appropriate mass ratios in an acidic medium (pH 2–3) were loaded onto the column for 2 min with a flow rate of 2.0 ml min⁻¹. When sodium or potassium is present at mass ratios of up to 2000 times that of the uranium, the relative errors are less than 10%. The effect of other ions namely cobalt(II), copper(II), lead(II) and nickel(II) in concentrations 20 times that of uranium, cause relative errors (RE) of about 20%, while in the presence of iron(III) at a concentration five times that of uranium, a 25% relative error is obtained. These interferences can be masked with CDTA.[15,24] It was found that the presence of CDTA up to 0.70% m/v in 0.1 mol l⁻¹ triethanolamine can be used without affecting the peak heights. When the quantity of CDTA exceeds 0.7% a decrease in peak height is obtained due to its complexation with uranium(VI). Tolerances of common ions are shown in Table 1. No interferences were found in the presence of REEs, titanium(IV), calcium(II) or magnesium(II).

Determination of Uranium

Peaks obtained by the recommended procedure are shown in Fig. 6. The standard curve ($y = 30.072x - 0.593$), is constructed by time- (or volume-) based calibration using standard solutions of 0.1, 0.5, 1.0 or 1.5 µg l⁻¹ of U. All yield the same linear curve up to 7 µg of U. Hence a particular quantity of uranium loaded onto the column from standard solutions of different concentrations always gives peaks of the same height (*e.g.*, peaks D, E and G in Fig. 6). Note that a series of different concentrations of standard solutions passing
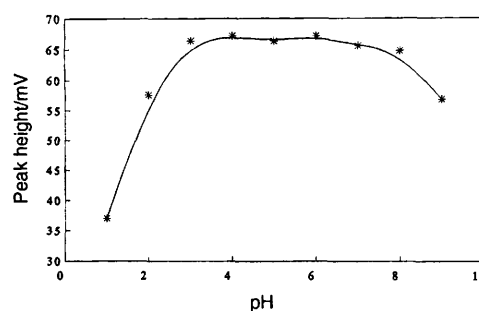

Fig. 3 Effect of length of preconcentration column on the FI peaks of U^{VI}–PAR complex.

Fig. 4 Effect of flow rate on the preconcentration of U^{VI}.

Fig. 5 Effect of pH of sample solution on the preconcentration of U^{VI}.

Table 1 Interfering effect of some ions on the response obtained from solutions containing 2 µg l⁻¹ U

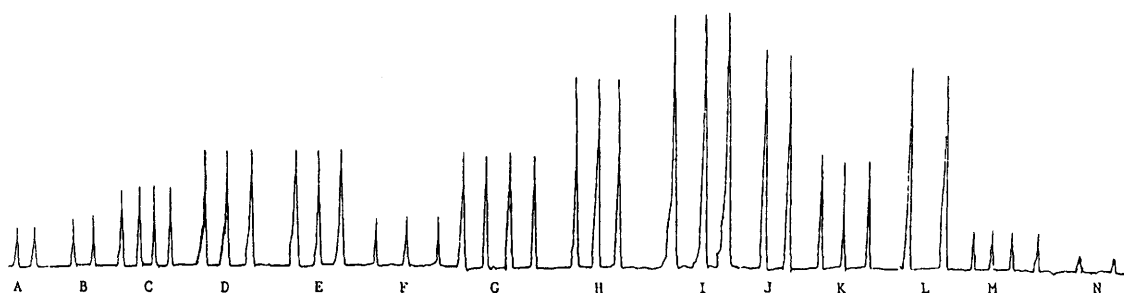| Ions	Ion : U^{VI}, mass ratio	RE (%)
Na, K	2000	<10.0
Ca, Mg	500	<5.0
Co^{II}, Cu^{II}, Ni^{II}, Mn^{II}, Cd^{II}, La^{III}, Al^{III}, Ti^{IV}, Th^{IV}, Sn^{IV}, W^{IV}	200	<5.0
Fe^{III}, Pb^{II}	50	<5.0
PO_4^{3-}, SO_4^{2-}, VO^{2+}	200	<5.0

Fig. 6 FI peaks for U^{VI}–PAR complex at various amounts of U^{VI} [peak label, mass loaded onto column in μg (concentration of standard solution used in μg l^{-1}, loading time in min)] with a flow rate of 1.8 ml min^{-1}: A, 0.6 (0.1, 3.5); B, 0.9 (0.1, 5); C, 1.4 (0.5, 1.5); D, 1.8 (0.1, 10); E, 1.8 (1.0, 1); F, 0.9 (0.5, 1); G, 1.8 (0.5, 2); H, 2.5 (1.5, 1); I, 3.9 (1.5, 1.5); J, rock sample (1 min); K, rock sample 2 (1 min); L, rock sample 3 (1 min); M, water sample 1 (32 min, flow rate, 2.5 ml min^{-1}); N, water sample 9 (40 min, flow rate, 4 ml min^{-1}).

Table 2 Determination of uranium in rock samples

	[U]/mg kg^{-1}	
Sample no.	FI	ICP-MS*
1	15.2	15.1
2	5.0	5.1
3	10.3	10.4
4	0.1	0.1
5	10.7	10.6
6	1.0	1.1
7	11.4	11.7

* Analysed by Institut fur Nukleare Entsorgungtechnik Kernforschungszentrum Karlsruhe, Germany.

Table 3 Determination of uranium in water samples by single determination and standard addition methods

	[U]/μg l^{-1}		
Sample no.*	Single determination	Standard additions	Recovery (%)
1	8.5	8.5	93.5
2	16.8	16.7	92.0
3	6.2	6.3	94.5
4	9.8	9.2	95.0
5	18.3	17.7	93.0
6	3.8	3.8	96.0
7	2.5	2.7	95.5
8	2.4	2.6	92.2
9	1.8	1.6	94.2

* 1–6, water in pools near tin mines; 7–9, underground water.

through the column for the same loading time exhibits a linear relationship similar to that of conventional calibration (peaks E, F and H). The flow rate regulated by the aquarium pump (1.2 ml min^{-1}) remained constant for at least 5 h. The detection limit (3σ) was 0.27 μg of U and the relative standard deviation was 2.1% for 2 μg of U ($n = 12$; 2 min loading time with a flow rate of 2 ml min^{-1} for a 1.0 μg ml^{-1} solution).

For rock sample solutions adjusted to pH 3–5 and analysed by the proposed method a throughput of at least 25 samples per hour can be achieved. The results are compared with those obtained by ICP-MS as shown in Table 2. Water samples were collected from underground and from water in pools near to tin mines in Chiang Mai, Thailand. Results are given in Table 3 together with results obtained by a method of standard additions: The recoveries are 92–96%.

Conclusion

The proposed method incorporates the advantages of on-line separation and preconcentration, namely speed, reagent economy, precision, selectivity, sensitivity, and high tolerance to interfering ions. A single standard solution can be applied for calibration. Requirements for determination of uranium in rocks and water are satisfied with low-cost instrumentation.

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