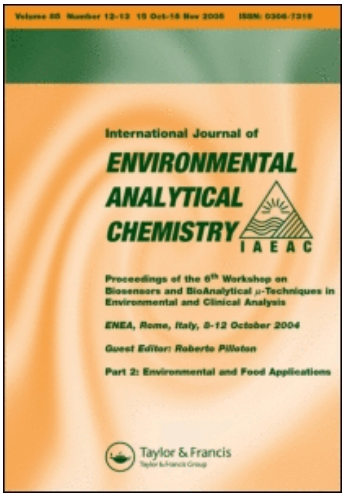

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Chromatography of Uranium on High-Performance Ion Exchangers

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The potential of high-performance liquid chromatography (HPLC) for the determination of U(VI) in ground waters and urine has been examined under a variety of HPLC experimental conditions. Conventional cross-linked and bonded-phase ion exchangers, both cation and anion, were studied with aqueous mobile phases containing tartrate, citrate, or α-hydroxyisobutyrate. The best chromatography was obtained on bonded-phase cation exchangers with an α-hydroxyisobutyrate eluent. The metal ions were detected either by visible spectrophotometry after a post-column reaction with a complexing reagent, or with a polarographic detector. Dectection after post-column reaction gave the best sensitivity; the detection limit ($2 \times$ baseline noise was 6 ng or 60 ng . ml^{-1} for 100 μl samples. In-line trace enrichment was used to decrease detection limits and linear calibration curves were observed in the ranges studied; 0.5 to 50 ng . mL^{-1} for ground waters and 25 to 400 ng . mL^{-1} for artificial urine.

KEY WORDS: Uranium, ion exchange, urine, ground water, trace analysis.

INTRODUCTION

Present methods available for the determination of U(VI) in aqueous solutions are often tedious and time consuming, especially in low ng . mL^{-1} concentration ranges. Such trace determinations are of particular importance to the uranium mining industry (monitoring of urine for permissable levels of uranium) and to nuclear waste-management studies (ground-water analyses). Recently, it has been shown that high-performance liquid chromatography (HPLC) offers considerable potential for the determination of trace quantities of metal ions[1–5]. Since classical chromatography is often used for sample cleanup prior to instrumental

analysis, sensitive and direct methods for the determination of metal species by HPLC have obvious attractive features. Anion exchange with coulometric detection has been used for the separation of U(VI)[1, 6, 7] but the detection limits reported would not permit analysis in the low $ng.mL^{-1}$ range. The purpose of this study was to examine the potential of high-efficiency anion and cation exchangers for the analysis of aqueous solutions for U(VI) in low $ng.mL^{-1}$ concentrations.

EXPERIMENTAL SECTION

Apparatus

A detailed description of the chromatographic system has been given elsewhere[5]. The system consisted of high-performance pumps (Model 6000A, Waters Associates, Milford, Mass. and SP 8700, Spectra Physics, Santa Clara, CA), a chemically-inert pump for sampling (CMP-1, Laboratory Data Control, Riviera Beach, FLA), and a constant-flow syringe pump (M314, ISCO, Lincoln, Nebraska) for the addition of the reagents for post-column reactions; the post-column reagent solution was added at the same flow rate used for the eluent. The sample-enrichment cartridge was a 4×30 mm guard column (Brownlee, Technical Marketing Associates, Mississaugna, Ontario, Canada) filled with a strong-acid bonded-phase exchanger. The eluate was monitored with either a variable-wavelength UV-visible detector (Tracor, Austin, Texas) or a constant-drop-size polarographic detector (EG & G, Model 310, Princeton NJ).

Reagents and Materials

The post-column reagent used for the detection of the metal ions was Arsenazo III (3-(2-arsonophenylazo-4, 5-dihydroxy-(2-arsonophenyl)-2, 7-naphthalenedisulfonic acid disodium salt); the concentration was $50\,ng.mL^{-1}$ and the pH was adjusted with nitric acid or acetic acid. All aqueous solutions were prepared with distilled water purified with a Milli-Q system (Millipore Corp., Bedford, Massachussetts); eluent and citric acid solutions were purified by constant-current electrolysis at 2.5 mA for 25 h at a Hg-pool electrode.

The 13 μm strong-acid cation and strong-anion resins (Aminex A-5 and A-27 respectively, BioRad, Mississauga, Ontario, Canada) were homogenized in an ultrasonic bath for 0.5 to 1 min and then slurry packed in water into 4×100 mm stainless steel columns at 34 MPa (5000 psi). The 5 μm bonded-phase cation exchanger (Nucleosil, Rainin Instrument Co., Brighton, Massachussetts) was slurry packed (in 1:1 water-isopropanol at 48 MPa) into glass-lined steel columns. Commercially packed 10 μm

bonded-phase cation and anion exchangers were also studied (Brownlee, Technical Marketing Associates, Mississauga, Ontario, Canada). The effect of the inorganics in urine on the determination of total uranium was studied by using artificial urine.[8] Ground-water samples were collected from experimental bore-holes at Chalk River Nuclear Laboratories. These samples were filtered through 0.8 μm filters and then made 0.01 mol.L^{-1} in nitric acid.

Sample Enrichment

Sample volumes of 1 to 10 mL were injected into a chemically-inert sampling valve and then pumped through the enrichment cartridge with a chemically-inert pump. Larger volumes were fed directly into the pump and then pumped through the enrichment cartridge. When the desired enrichment was achieved the cartridge was valved into the eluent and then enriched components were back-flushed onto the column.

RESULTS AND DISCUSSION

Column Studies

Uranium (VI) ions were retained strongly by the styrenedivinylbenzene strong-anion resin studied, Aminex A-27. Eluents containing large concentrations of salts were required for elution of U(VI) and these eluents, as well as similar eluents used in other studies on the same[7] or similar anion resins,[1] interfered with the post-column reactions used for the detection of the eluted U(VI). This strong adsorption and the fact that the U(VI) peaks were very broad, precludes the use of this type of resin. The bonded-phase anion exchanger did not require as strong an eluent but the peaks were still unacceptably broad for all of the eluents studied.

Good separations were obtained with cation-exchange resins and the eluents used were compatible with the post-column reactions used for detection. For the styrenedivinylbenzene resin, Aminex A-5, however, detection limits were poor due to the elution of the U(VI) as a broad tailing peak. Optimum results were obtained with the bonded-phase cation exchangers; peak shapes were more symmetrical and column efficiences were in the range of 0.2 to 0.3 mm at flow rates of 1 to 2 mL.min^{-1}. Slightly better separations were obtained with the smaller particle exchanger. A study of the effect of temperature on column efficiency showed that there was no appreciable gain in column efficiency over the range of 19 to 75°C.

Different combinations of pH and complexing reagents (citrate, α-hydroxyisobutyrate, tartrate) were used for the elution of U(VI) from the

bonded-phase cation exchangers. Optimum separations were obtained with 0.15 mol.L^{-1} α-hydroxyisobutyrate at pH ≃ 4.5.

Detection

Three reagents were examined for the detection of U(VI) after a post-column reaction: Arsenazo III, PAR (4-(2-pyridylazo)-resorcinol), and BrPADAP (2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol). Arsenazo III was used almost exclusively since it gave low background-absorption at the wavelength (650 nm) used for detection of the U(VI)-Arsenazo III complex, was readily soluble in water, gave a large absorptivity for the U(VI) complex (~50,000), and was selective for U(VI) in the pH range of 1 to 2. PAR also gave satisfactory results but was not as selective or sensitive. The main disadvantage of BrPADAP was its low aqueous solubility.

The other metal ions that exhibited an appreciable reaction with Arsenazo III under the separation and detection conditions used, were Fe(III), Zr(IV), Th(IV), and the lanthanides. The lanthanides, Fe(III), and Zr(IV) were eluted at or near the solvent front before U(VI), and Th(IV) was eluted after U(VI). For maximum selectivity Arsenazo III was normally prepared in 0.25 mol.L^{-1} nitric acid but the reagent slowly decomposed under these conditions and an acetate buffer (pH 4) was used if maximum selectivity was not required. The detection limit for U(VI) with this post-column reaction system was 6 ng.

Sensitive detection of U(VI) with the polarographic detector, operated in the reductive mode, was hampered by the reduction of oxygen which rapidly diffused through Teflon lines into the degassed eluents. An example of one of the chromotograms obtained with this detector is shown in Figure 1; the mechanism for the retention of the oxygen on this bonded-phase exchanger is unclear. Further increases in signal-to-noise could undoubtably be obtained if eluents were prereduced prior to the sample-injection point[9] or, if the HPLC system was placed in an inert atmosphere.[10] The detection limits (twice peak-to-peak noise) were 12 ng for Fe(III) and 80 ng for U(VI); peak-to-peak noise was ~2 nA. Since the sensitivity of the post-column reaction system was superior to that of the polarographic detector, the post-column reaction was used in all further studies.

Calibration and Enrichment

Linear calibration curves were obtained for the Arsenazo III detection system over the range studied, 25 to 2000 ng U(VI). The relative standard

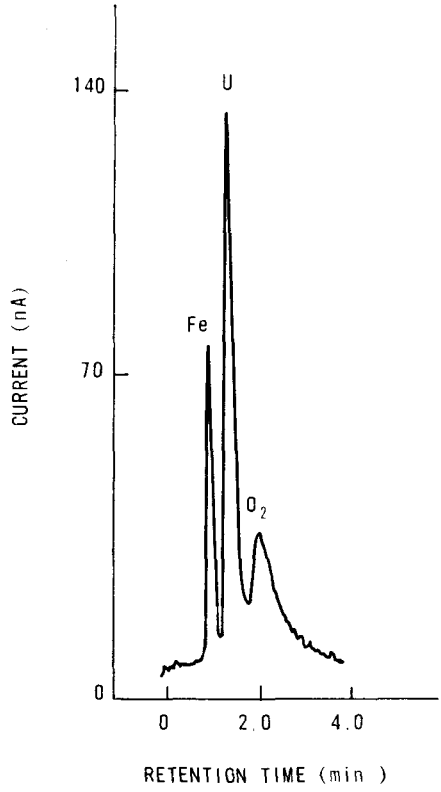

FIGURE 1 Chromatogram obtained with polarographic detector. Experimental conditions; Sample, 2 μg U(VI) and 0.2 μg Fe(III) degassed with He, residual $0_2 \sim 200$ ng; Mobile phase, 0.2 mol.L^{-1} α-hydroxyisobutyrate at pH 4.6; Flow-rate, 2.5 mL.min^{-1}; Column, 4 x 250 mm Brownlee bonded-phase cation exchanger, 10 μm; Detector, -0.650 V, 1 drop (small).s^{-1} sampled DC mode.

deviation for multiple injections of ~ 700 ng U(VI) was $< 1\%$. With direct injection the minimum detectable concentration of U(VI) was ~ 60 ng.mL^{-1}, Accurate analysis in the low ng.mL^{-1} range required sample enrichment and an in-line sample-enrichment cartridge was used for this purpose. Sample additives (tartrate, citrate and α-hydroxybutyrate) previously used to keep metal ions in solution prior to sample enrichment[4,5] caused premature elution of U(VI) from the enrichment cartridge but good recoveries were obtained when the samples were made 0.01 to 0.1 mol.L^{-1} in nitric acid; losses were observed for acid concentrations below 0.01 mol.L^{-1}.

Quantitative recoveries were obtained for enrichment of sample sizes up to 10 mL; sample losses of up to 25% were observed for 100 mL samples. For 10 mL samples linear calibration curves were obtained in the range studied, 2 to 40 ng.mL^{-1}, and the detection limit was ~0.5 ng.mL^{-1}. With 1 mL samples linear calibration curves were obtained from 25 to 400 ng.mL^{-1} and the detection limit was ~6 ng.mL^{-1}.

During these studies double peaks were sometimes observed when U(VI) solutions were enriched but not with direct sample injection. The results of studies with a number of enrichment cartridges and silica-gel columns showed that the double peaks were due to the presence of mixed ion-exchange sites, silanol and sulfonic acid groups. It is believed that the nitric acid in the samples caused cleavage of the Si-O and/or Si-C bonds in the bonded phase to give free silanol groups; the results of studies with silica columns showed that these groups can cause increased retention of U(VI) under the experimental conditions used. The slow degradation of the bonded phase limited the useful life of the enrichment cartridge to approximately two weeks.

Urine Analysis

Urine contains large concentrations of organics which will often plug HPLC columns if samples are injected directly onto the columns. Since destruction of these organics would likely be a requirement for successful HPLC analysis, attention was focussed on the effects of the inorganic components. An artificial urine solution[8] was used for these studies.

Linear calibration curves were obtained over the range studied, 25 to 2000 ng, for direct injection of U(VI) dissolved in artificial urine. Similar results were also obtained for the enrichment of 1 mL samples over the range 25 to 400 ng.mL^{-1}; the detection limit for these 1 mL samples was ~6 ng.mL. For both sample sizes U(VI) peak areas were the same as those obtained for similar samples prepared in distilled-water. For enrichment of larger samples of artificial urine, however, losses were observed. Studies of the effects of the individual components in the artificial urine showed that the majority of the sample loss was due to the formation of phosphate complexes with U(VI).

Ground-Water Analysis

Linear calibration curves were obtained for enrichment of 10 mL samples of spiked ground water in the range studied, 0.5 to 50 ng.mL^{-1} U(VI), and preliminary studies indicated that larger sample sizes could be used.

The large concentrations (relative to U(VI)) of Fe(II) and/or Fe(III) in ground waters can interfere with the determination of small concentrations of U(VI) unless ascorbic acid is added (10^{-2} mol.L^{-1}) to keep iron in the Fe(II) state which does not react with the detection reagent under the experimental conditions used. An example chromatogram for a ground-water blank and a spiked sample are shown in Figure 2.

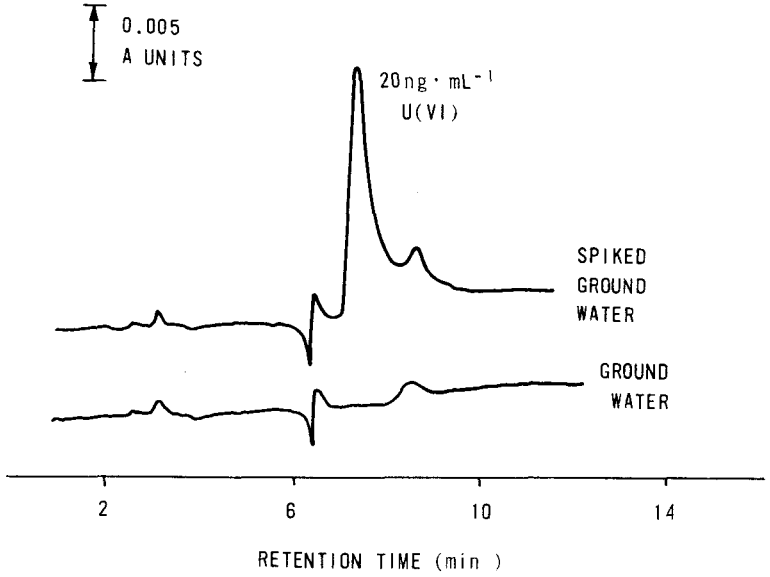

FIGURE 2 Separation of U(VI) in ground water after enrichment. Experimental conditions; Samples, 10 μL of ground water 0.01 mol.L^{-1} in ascorbic acid and 0.1 mol.L^{-1} in nitric acid; Mobile phase, gradient of 0.12 to 0.20 mol.L^{-1} α-hydroxyisobutyrate (pH 4.5) over 20 min at 1 mL.min^{-1}; Column 4 × 250 mm Brownlee bonded-phase cation exchanger, 10 μm; Enrichment cartridge, 4 × 30 mm bonded-phase cation exchanger; Detection, absorption at 650 nm after post-column reaction with Arsenazo III.

When ground waters (and especially surface waters) are analyzed by the above method the results correspond to labile metal species only, and if the concentration of these labile species is of interest then the samples should be analyzed as soon as they are acidified. Standard-addition techniques will not guarantee accurate results because the chemical equilibria involved in natural waters is very complex and often extremely slow for a significant portion of the total metal ions.[11] For the determination of total metal ions, the organic matter should be destroyed by acid digestion, UV radiation, or γ-radiation.[12]

CONCLUSIONS

These studies have shown that bonded-phase cation exchangers can be used for the trace enrichment and HPLC separation of U(VI) in aqueous solutions. Studies with artificial urine have indicated that enrichment is of limited use for samples containing large concentrations of salts. For many other samples, such as ground water, however, this technique offers a rapid, selective, and sensitive method for the determination of U(VI).

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