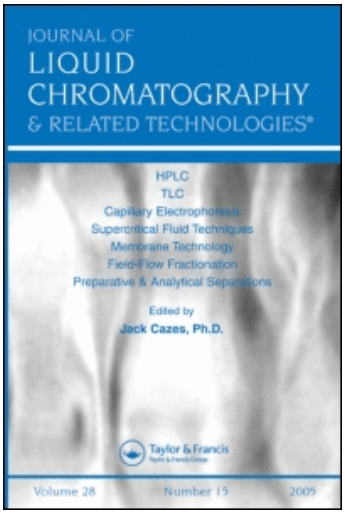

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A Screening Protocol for the Direct Determination of Low PPB Levels of Uranyl Cation Using Arsenazo III and Capillary Electrophoresis

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A SCREENING PROTOCOL FOR THE DIRECT DETERMINATION OF LOW PPB LEVELS OF URANYL CATION USING ARSENAZO III AND CAPILLARY ELECTROPHORESIS

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ABSTRACT

Capillary electrophoresis is used as a screening protocol for the determination of uranyl ion complexed with Arsenazo III. Long sample plugs are injected and stacked to narrow zones. Capillary column inner diameter, running buffer constituents and concentrations, effective column length and injected sample plug length are optimized and discussed. A limit of detection of 10 ppb is achieved with a linear dynamic range of nearly 3 orders of magnitude in concentration injected. Analytical figures of merit are presented and river water samples are analyzed.

INTRODUCTION

There is interest in the geological, environmental and bioassay fields in a fast and simple analysis tool for uranium due to its presence in water and various mineral samples (1). The toxicity of uranium and its common use in nuclear power stations and nuclear weapons creates the need for a cost effective analysis method (2). Numerous methodologies have been developed for the analysis of uranium including time resolved laser fluorescence (1,3-5), isotope dilution mass spectrometry (6), laser ablation - inductively coupled plasma atomic emission spectrometry (7), and flow injection analysis (8). Most of these are expensive, time consuming and instrumentally complicated. Simpler methods have been effective which depend on spectrophotometry and require the use of masking agents or a separation such as HPLC, ion chromatography or extraction; however, most of these methods use large volumes and are slow (5,9-15).

Capillary electrophoresis (CE), with its high efficiency, speed and small sample and reagent volume requirements, can be more cost effective and time efficient than the aforementioned methodologies. The small capillary diameters are very effective in dissipating Joule heating; thus, large fields can be used to decrease the separation time and the plug-like flow leads to highly efficient separations. Over the past few years, CE has become a very useful separation tool. The high efficiency and speed make it an ideal choice for many applications. However, the diminutive size of the capillary diameter results in poor concentration detectability (9,16-19). Several approaches have been utilized to improve detection limits including sample pre-concentration and non-traditional capillary or detector cell geometry (19,20). Furthermore, sensitive detection methods

such as radiochemistry, fluorescence or electrochemistry have been utilized in an effort to improve CE detection limits (19,20).

Sample stacking is one of the simplest ways to concentrate a sample and improve detectability. In this approach, the analyte is dissolved in either water or low ionic strength buffer and a very large sample volume is injected. The lower ionic strength in the sample region results in a higher field. Thus, the sample ions in the injected volume will migrate at a high velocity. As the sample ions encounter the interface between the sample and relatively high ionic strength running buffer, velocity is reduced due to the presence of a lower field within the running buffer. This causes the analytes to stack into a narrow band. Subsequently, the analytes are separated by free solution CE (16-19). Both anions and cations can be analyzed by this technique. However, field inhomogeneities between the sample plug and the running buffer causes the electroosmotic flow velocity (v_{eo}) to be different between the two regions. This produces a hydrostatic pressure, resulting in a parabolic flow profile which can broaden the solute band and negate the concentrating effect. Longer sample plug lengths or greater disparity between the sample and running buffer ionic strengths will augment the dispersive effects of parabolic flow; thus, an optimum exists between sample stacking and the deleterious effects of band broadening (16-18). Reference 19 is a good general review article concerning stacking and other methods of sensitivity enhancement. Reference 16 provides a mathematical treatise of stacking.

A variety of reagents can be used to form a complex with U(IV) or U(VI) for use in spectrophotometric analyses including PAR, PAN, malachite green and Arsenazo III

(2,14,21-23). Arsenazo III is the most widely used reagent for the determination of uranium. There is a large red shift (about 140 nm) in the lowest energy absorbance band of free Arsenazo III when it forms a metal complex. Thus, excess Arsenazo III present in the system will have a very low background at the complex maximum (2,5,12,13,21-23). Typical spectra appear in Figure 1. Unfortunately, Arsenazo III is not selective and forms complexes with many other metals such as Th, Zr, rare earths, Ba, Sr, S, Pd, Sc, Pb, Fe III, Cu, Ca, Al (12,13,21-23). Solution pH plays an important role in complex formation; the optimum for uranyl ion - Arsenazo III formation is pH 1-4. At these moderately low pH values, some of the aforementioned metals do not form complexes. However, the general lack of selectivity still renders a separation necessary.

The method presented herein uses field amplified CE (18,24) for a fast, simple and sensitive determination of the uranyl cation. A wide variety of experimental parameters are assessed and discussed. These include capillary column inner diameter (i.d.), effective column length (L_{eff}), running buffer composition and concentrations and sample plug lengths. Analytical figures of merit and analyses of local water samples are presented.

EXPERIMENTAL

Concentrated stock solutions of uranyl nitrate hexahydrate (Mallinckrodt, Paris, KY) and 2,2'-(1,8-dihydroxy-3,6-disulfonaphthylene-2,7-bisazo) bisbenzenearsonic acid (Arsenazo III) (Aldrich, Milwaukee, WI) were made in water and diluted to the appropriate concentration as desired. Sodium phosphate, sodium borate,

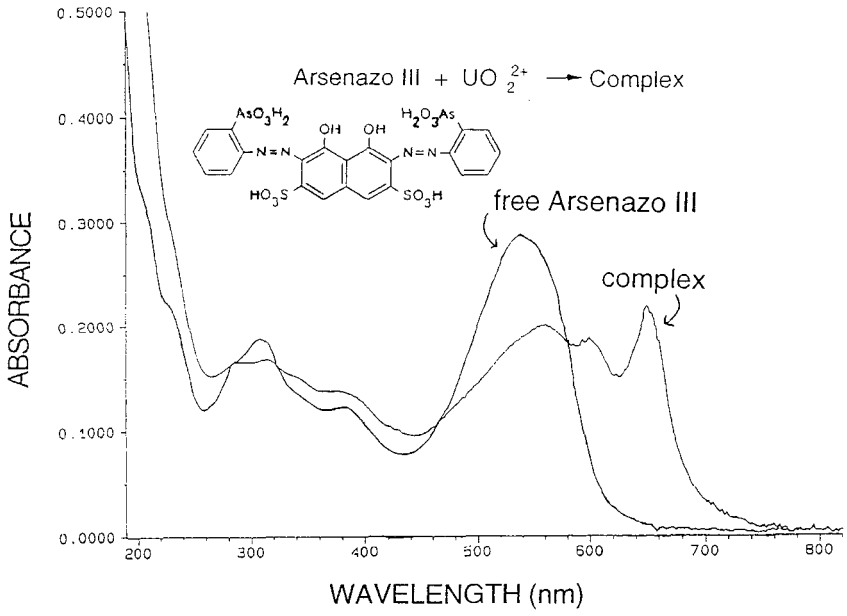

FIGURE 1: Absorbance spectra of (a) free Arsenazo III and (b) Arsenazo III-uranyl complex.

sodium chloride, perchloric acid and methanol were obtained from Sigma (St. Louis, MO) and utilized as needed. Distilled water was purified by a Millipore MilliQ filter (Bedford, MA).

The experimental apparatus has been described in detail elsewhere (25). Briefly, an SSI (Science System Inc., State College, PA) model 504 absorbance detector was used at 650 nm. Fused silica capillaries (50, 75 μm i.d., 360 μm o.d.) were obtained from Polymicro Technologies, Inc. (Phoenix, AZ) and extended light path capillaries (ELP) (25 μm i.d. with 125 μm window, 360 μm o.d.) were purchased from Hewlett Packard (Palo Alto, CA). Running voltages were provided by a Hipotronics (Brewster, NY) high voltage power supply. Electropherograms were recorded using a chart recorder and

a PE Nelson integrator Model 1020 S (Perkin-Elmer Corp, Cupertino, CA).

Prior to initial use, each column was pre-treated by sequentially washing the capillary with 10 mM NaOH, water, 10 mM HCl and water at 20 minutes each. The column was then filled with the running buffer and electrokinetically pumped for 20 minutes to equilibrate the column. Hydrostatic injections were made by elevating the column inlet for a given time. Once an injection was performed, the capillary was returned to the running buffer vial and a negative voltage was applied for the separation (cathodic inlet, anodic outlet). The injected plug length was estimated by determining the linear velocity of the sample during the injection process (v_{inj}). This was accomplished by continuously injecting a Arsenazo III - uranyl complex. Linear velocity is then given by L_{eff}/v_{inj}. The following rinse procedure was utilized between separations: 5 minutes 10 mM NaOH, 3 minutes water, 2 minutes running buffer.

The samples used in this work contained uranyl cation, 0.1 mM Arsenazo III, and 0.1 mM $HClO_4$ diluted to volume with water. When the running buffer contained methanol, the sample also contained 10% methanol.

RESULTS AND DISCUSSION

Stacking Mechanism

In this method for uranyl ion analysis, relatively long sample plugs (between 1-8 cm) were injected and subsequently stacked in a manner similar to that described by Chien and Burgi (17-19,24). The negatively charged complex has an electrophoretic velocity greater in magnitude

and opposite in direction than the v_{eo}. Thus, the sample buffer is backed out into the running buffer reservoir as the analyte stacks at the moving boundary between the sample and running buffer. This is depicted in Figure 2.

In the experiment depicted in Figure 2, a long sample plug (13 cm) was injected and a negative voltage was applied. A very long sample plug was utilized to elucidate the stacking mechanism. This long sample plug may overload the system and contribute to the triangular shape of the second peak in the electropherogram shown in Figure 2e. The effective column length was only 9 cm; therefore, the sample extended past the detector at the time the voltage was applied (see Figure 2a). Initially, the field and hence the v_{eo} within the sample zone is greater than in the running buffer due to the lower ionic strength in the sample (see Running Buffer Optimization below). However, the net velocity of the complex is greater than the v_{eo} and sample ions begin to migrate towards the anode and stack at the running buffer - sample interface.

The inhomogeneity of the v_{eo} between the two zones causes a hydrostatic pressure to form (see Figure 2b). The velocity due to this hydrostatic pressure makes up the difference between the two v_{eo}s. The analyte stacks at the boundary while the hydrostatic pressure and v_{eo} push the sample plug toward the capillary inlet. The injection plug length decreases and its ionic strength increases causing the field to decrease in the sample zone. Thus, the velocities of both the v_{eo} and complex decrease in the sample zone and increase in the running buffer region. The complex tries to migrate against the v_{eo} but is unable to do so in the running buffer due to the hydrostatic flow. The portion of the sample which extended beyond the detector is swept quickly past the detector as shown by the first peak (at approximately 30

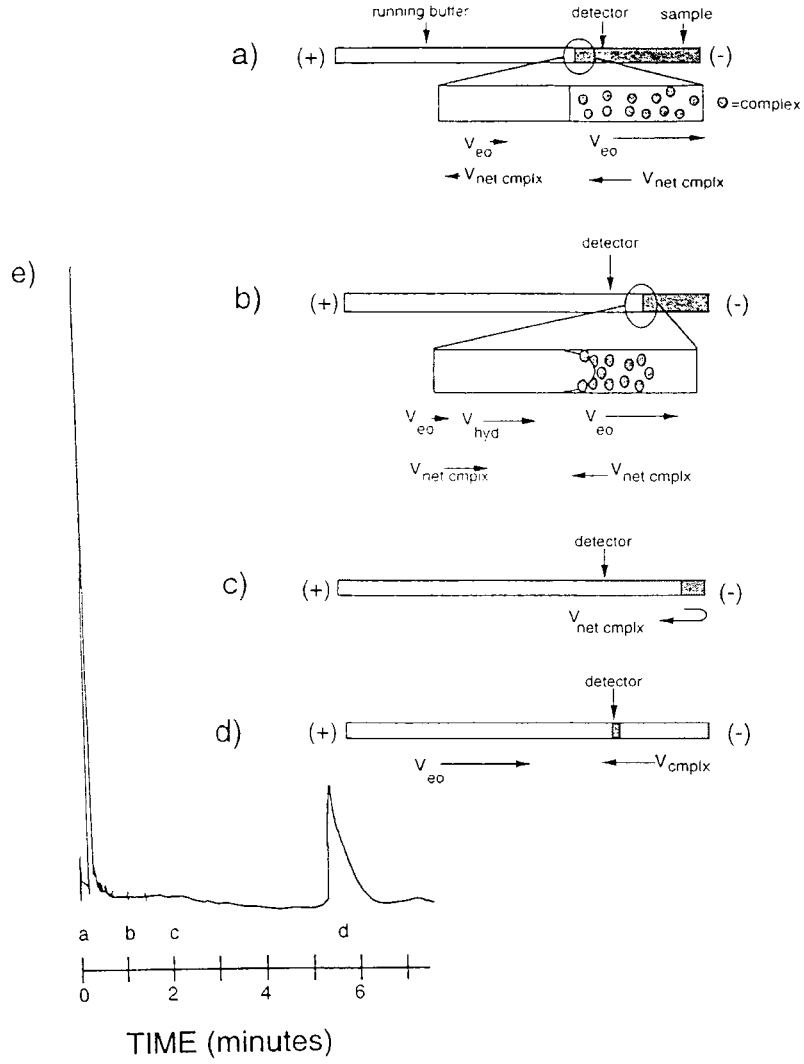

FIGURE 2: Depiction of the stacking mechanism: (a) voltage initially applied, (b) analyte stacking and removal of sample buffer, (c) equilibration of the v_{eo} within the running buffer and sample zones: analyte reverses direction, (d) stacked analyte passes the detector, (e) electropherogram from this experiment. Experimental conditions: L_{eff} = 9 cm, i.d. 50 μm, applied field of 375 V/cm, injected plug length of 13 cm. See Table 1 for running buffer composition.

sec) in the electropherogram resulting from this experiment (Figure 2e).

By the time the sample plug nearly reaches the end of the column (Figure 2c), the hydrostatic pressure has diminished and the v_{eo}s of the sample and running buffer zones have become nearly equal. The analyte is now able to migrate against the v_{eo} (i.e., it reverses direction) and eventually migrates past the detector (Figure 2d). Considering the complexity of these electrophoretic processes, it is not surprizing that the analyte band is asymmetric and not particularly efficient (see Figure 2e). In this experiment using a very short effective capillary, the Arsenazo III system peak and the complex show no separation (see below).

System Peak

Typical electrophoretic peak profiles are presented in Figure 3 in which the analyte appears as a shoulder on the system peak. Resolution between the system peak and the shoulder is dependent on the L_{eff} and is discussed below. A capillary with L_{eff} = 40 cm is used for this experiment. To assure complete complexation of uranyl ion and any interfering metals present, excess Arsenazo III is added to the sample. Arsenazo III is negatively charged and exhibits a mobility only slightly greater than that of the uranyl ion - Arsenazo III complex. Although the absorbance of free Arsenazo III at 650 nm is minimal (Figure 1), stacking increases the concentration sufficiently to generate the system peak illustrated in Figure 3a. The shoulder on the system peak (uranyl ion - Arsenazo III complex) grew with the concentration of the uranyl cation in the sample until it swamped out the system peak.

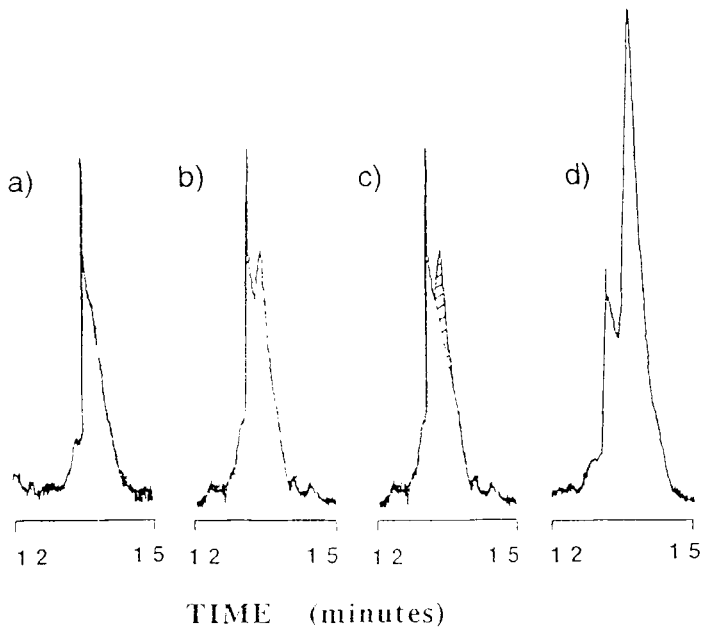

FIGURE 3: Electrophoretic peak profiles: (a) system peak, (b) 25 ppb injected uranyl complex, (c) 25 ppb injected uranyl complex with analyte peak shaded, (d) 200 ppb injected uranyl complex. See Figure 2 for experimental conditions.

Many approaches were attempted to minimize the contribution of the system peak by increasing efficiency, improving the resolution between the system and analyte peaks, or decreasing the magnitude of the system peak. One approach was to improve efficiency by increasing the stacking effect. Increasing the difference in ionic strength between the sample and the running buffer will enhance the stacking phenomenon. Unfortunately, at some point, band broadening from hydrostatic flow became excessive. Moreover, as the running buffer ionic strength was increased, efficiency decreased due to Joule heating. Another approach

was to adjust system retention to increase resolution. Methanol was added to both the sample and the running buffer to decrease Joule heating (increase efficiency) and to slow v_{eo} so that slight differences between the mobilities of the system peak and the analyte peak could be enhanced leading to improved resolution. Unfortunately, this had minimal effect on efficiency and resolution. The concentration of Arsenazo III in the running buffer did not have a noticeable influence on the magnitude of the system peak. Ultimately, it was determined the resolution between the system and analyte peaks appeared to be best when longer columns were used (see "Optimum Column Length and Injection Plug Length" below).

Running Buffer Optimization

Optimum running buffers had to be determined for each column i.d. Each buffer consisted of Arsenazo III, perchloric acid, sodium phosphate, sodium borate and sodium chloride in various concentrations. Methanol was also included on occasion.

A common CE buffer (26,27) of sodium phosphate and sodium borate was included in each running buffer. However, the concentration usually used (10 and 6 mM, respectively) interfered with the complex formation between Arsenazo III and UO_2^{2+}. A tenfold decrease in concentration (i.e., 1 and 0.6 mM, respectively) appeared to cause no interference, as determined by UV/Vis spectrophotometry, and was thus used in all experiments. An acidic medium is required for the formation of the Arsenazo III - uranyl complex and there was little difference in the absorbance of the complex between 10 and 100 mM $HClO_4$. Thus, the 10 mM concentration was included in each running buffer resulting in a pH of 2.7.

Arsenazo III and sodium chloride were doped into the running buffer to prevent complex dissociation and to improve stacking. However, excessive amounts of Arsenazo III resulted in a high optical background while high salt concentrations produced excessive Joule heating. Therefore, an optimum concentration of each component was determined. These optimum concentrations varied with the i.d. of the capillary. Smaller diameter capillaries were able to tolerate higher salt concentrations and dissipate the heat generated better than larger capillaries. Two concentrations of Arsenazo III were tested for each column i.d. - 0.01 mM and 0.1 mM for column i.d.s of 75, 50, and 25 (ELP) μm. For the 75 μm i.d. column, sodium chloride concentrations of 10, 50, and 75 mM were added to each Arsenazo III concentration. For the 50 and 25 (ELP) μm i.d. column, salt concentrations of 50, 75, and 100 mM were tested. Once it was determined that 0.1 mM Arsenazo III was best for the ELP capillary, additional salt concentrations of 125, 150, and 200 mM were also used. Table 1 lists the optimum Arsenazo III and sodium chloride concentrations for each column with approximate limits of detection (LODs) as experimentally determined. It is unknown why the optimum Arsenazo III concentration varied with the capillary employed. The optimum salt concentration varied as expected; that is, smaller i.d. capillaries tolerated higher salt concentrations. In each case, the thermal load is near the limit of causing significant thermal dispersion (28).

By adding methanol to the running buffer, the current could be reduced and higher fields could be employed to reduce separation time. The LODs represent a signal/noise (S/N) of 3 as described below. The LODs follow a trend opposite to that expected; the shortest optical path length has the best LOD and the longest optical path length has the

TABLE 1
Optimized Running Buffers[a]

Column (μm)	Arsenazo III (mM)	NaCl (mM)	L_{eff} (cm)	LOD (ppb)	Thermal load (W/m)	Mobility (cm/min)
75	0.01	50	40	33	0.96	1.8
50[b]	0.01	75	31	25[c]	1.3	2.3
25 ELP	0.1	150	50	100	1-1.3	4.3

a All running buffers include 10 mM $HClO_4$, 1 mM sodium phosphate, and 0.6 mM sodium borate
b Optimum running buffer included 10% MeOH
c Approximate LOD in a L_{eff} = 31 cm column. Can detect 10 ppb in a L_{eff} = 50 cm column.

worst LOD. This is probably an outcome of the complicated stacking process and the presence of the only partially resolved system peak.

Sensitivity and Detectability

Due to the presence of the system peak (Figure 3a), determination of the peak area was complicated. As shown in the figure, the peak shape changes with concentration. At low levels of analyte, the complex peak is a shoulder on the system peak. This is shown for a 25 ppb UO_2^{2+} profile in Figure 3b and the appropriate portion shaded in for Figure 3c. As the analyte concentration increases, the shoulder grows as shown in Figure 3d. From 25 - 100 ppb, the area of the individual peak was determined by manually skimming the tail of the system peak (see Figure 3c). For higher concentrations, the average blank signal was subtracted from

the total peak area to determine the peak area of the complex.

A reproducibility study was conducted by injecting the blank and a 25 ppb UO_2^{2+} solution six times in a L_{eff} = 31 cm, 50 μm i.d. capillary and performing the separation. The average peak area of the blank was 44 arbitrary units with a coefficient of variation (CV) of 8.5%. The average peak area of the 25 ppb UO_2^{2+} peak, skimmed from the system peak as shown in Figure 3c, was 1.9 arbitrary units with a CV of 51%. A CV of 50% corresponds to a S/N of 3 (29). Thus, the LOD for this system is very close to 25 ppb. Lower concentrations can be detected if longer columns are used to improve resolution; however, separation time increases. Although a reproducibility study was not performed by using a longer column (L_{tot} = 60 cm, L_{eff} = 50 cm), 10 ppb could be seen as a shoulder as easily as the 25 ppb peak could be seen in the shorter column. Thus, the LOD in the longer column is approximately 10 ppb.

A calibration curve was constructed from duplicate injections that exhibited a linear dynamic range of 2.8 orders of magnitude in concentration injected (see Figure 4). This linear dynamic range may be extended by increasing the concentration of Arsenazo III in the sample. However, increasing the Arsenazo III concentration in the sample will increase the system peak.

Optimum Column Length and Injection Plug Length

In screening applications, rapid separation times are necessary to increase throughput. In this study, longer column lengths have better resolution and LODs at the

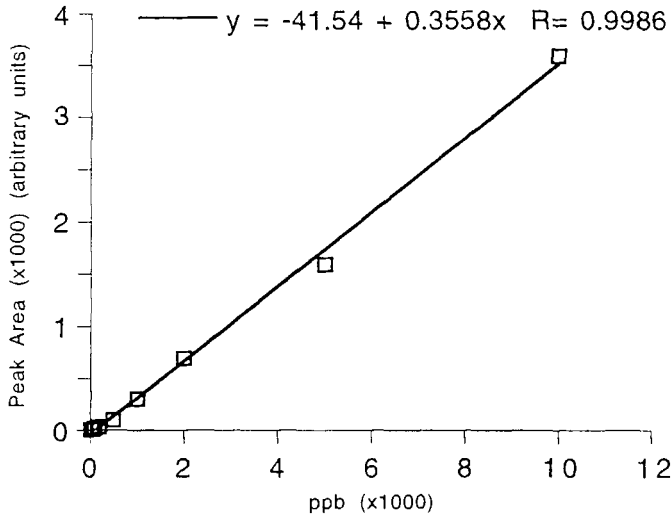

FIGURE 4: Calibration curve for uranyl cation. Injected plug length is 5.8 cm, L_{eff} = 31 cm. See Figure 2 for other experimental conditions.

expense of separation times (see Table 2). Therefore, various column lengths were evaluated using the 50 μm i.d. column to find the optimum between resolution and time. At very short column lengths (L_{eff} = 9 cm), resolution was completely lost. Thus, an effective length of 31 cm was used for most experiments, as it represented a reasonable compromise between resolution and separation time.

The LODs listed in Tables 1 and 2 were determined using optimum injection plug lengths. By injecting more material into the column, LODs should be improved provided efficiency and stacking remain reasonable. The best injection plug lengths were determined for each capillary with its optimum running buffer (see Table 1) by increasing the injection plug length until excessive band broadening occurred. The

TABLE 2
Optimization of Effective Column Length and Injection Plug Length

Column diameter (μm)	Total column length (cm)	Effective column length (cm)	Optimum injection plug[a] (cm)	Approx-imate LOD (ppb)	Separation time (min)
75	50	40	3.5	33	22
50	60	50	7.8	10	20
	40	31	5.8	25	13
	40	9	3.9	200	6
25 ELP	60	50	1.6	100	12

a Maximum injected plug length before excessive band broadening occurs

optimum plug length (see Table 2) is the best compromise between band broadening and improved LOD.

Interferences and Selectivity

A common limitation in uranyl cation analysis is inadequate selectivity. At a pH of 2.7, Arsenazo III forms complexes with several different metals including Sc, Y, Ln, Bi, Pb, and Fe(III) (12,13,21-23), thus requiring that extractions, pH adjustments, masking agents or some separation be performed. CE proved to be extremely selective in this work. The complex formed between the uranyl ion and Arsenazo III was negatively charged while most other complexes were neutral or positively charged. When the metals expected to be present in real samples (i.e., Hg, Pb, or Ca) were added in excess, no additional peaks were observed, and the uranyl - Arsenazo III peak remained unchanged.

To assess the effects of a "dirty" sample on LOD, water taken from the Pigeon River (Cocke County, TN) was filtered through a 8 μm polycarbonate filter to remove particulate matter and analyzed. Arsenazo III - metal complexes formed at this pH are purple or bluish in color. All samples made with the Pigeon River water were a bright blue color, indicating a high level of complexes of various metals; yet these complexes did not interfere with the uranyl ion determination. A 50 μm i.d., L_{eff} = 50 cm capillary was used for the analysis. A standard addition calibration curve was constructed which was linear with a coefficient of regression of 0.998. No UO_2^{2+} was found in the Pigeon River water. The river water matrix did not interfere with detectability of low concentrations of added uranyl ion (10 ppb).

An additional water sample was taken from Poplar Creek (Oak Ridge, TN) below the Oak Ridge Y-12 Plant and analyzed using the 50 μm i.d., L_{eff} = 50 cm column. Each of the samples made from this water was again blue showing a high concentration of complexed metals. Based on the standard addition method, about 18 ppb UO_2^{2+} was found in the river water. This was the median as reported in the 1995 Y-12 National Pollution Discharge Elimination System Report (30). Collection occurred after a rain shower which has the effect of stirring up the sediment and increasing the uranyl cation concentration.

CONCLUSIONS

This method of uranyl cation analysis is simple, rapid and inexpensive to perform. It has a comparable separation time and LOD with an HPLC method (9) and requires far less

volume of sample and running buffer. However, detectability was limited by the presence of a large system peak. Attempts to increase resolution between the system and analyte peaks were of limited success. Improvements in detectability could be made if the system peak could be removed. Some reduction in the system peak may be accomplished by monitoring the separation at two wavelengths - one at the maximum absorbance of Arsenazo III (about 540 nm), the other at the maximum absorbance of the complex (about 650 nm) - followed by a mathematical manipulation to reduce the effect of the free Arsenazo III background (see Figure 1). Unfortunately, this solution could not be evaluated due to limitations of the equipment. Nevertheless, the method presented herein is a good screening protocol for the uranyl ion at low ppb concentrations that exhibits a high degree of selectivity.

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