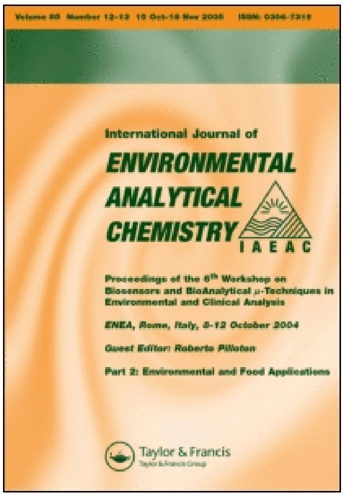

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Preconcentration of Uranium for X-ray Fluorescence Determination on Chemically-Modified Filters

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A quantitative preconcentration technique for uranium as the uranyl ion is described. The method utilizes a silica-cellulose filter material (Whatman SG-81, 20% w/w silica gel) which has been modified by silylation with N-β-ethyl-γ-aminopropyl trimethoxysilane (Dow-Corning Z-6020). The uranyl solution is extracted after adding ammonium carbonate to form the tris-carbonato uranyl-complex ($UO_2(CO_3)_3^{4-}$). This complex forms a strong ion-pair with the protonated diamine group bonded to the silica portion of the filter. The extraction is effective in the pH range 6–8 and recovery was observed to lie in the range of 70–95% as the concentration was varied from 10 ppm to 0.5 ppm. The low recovery at high concentration is attributed to loading the functional sites. The uranium content of synthetic samples and extractive mining process samples has been determined using x-ray fluorescence measurements on the filter following extraction. The current procedure shows a 3.5% relative standard deviation and a lower limit of detection of 5.4 μg U from a 25 mL sample (0.2 ppm).

KEY WORDS: Uranium, preconcentration, x-ray fluorescence.

INTRODUCTION

The determination of the concentration of uranium in aqueous solution is important in the mining industry in such applications as hydrogeochemical exploration, solution-mining process control and environmental monitoring.[1] X-ray fluorescence spectrometry (XRF) is frequently employed in the determination of uranium because of the ease and convenience of the method; however, the solutions generally contain only trace level concentrations of uranium and thus a preconcentration step is needed prior to analysis. A method to concentrate uranium onto a suitable solid substrate in a single step is desirable. Recently a method for enrichment of trace metals was described which employs a simple filtration of the aqueous solution through a chemically-modified filter.[2] The method utilizes a silica-cellulose filter chemically-modified by bonding a silane-dithiocarbamate to the silica surface. The aqueous sample is continuously cycled through the filter in a closed-loop flow system. It was suggested by the authors that this method is applicable to the preconcentration of trace levels of uranyl ion; however, no data was reported.

This study deals with the extraction and preconcentration of uranyl ions (UO_2^{2+}) from aqueous solutions using a similar technique. The extraction and subsequent enrichment of uranium onto the filter is accomplished by proposed ion-pairing of the tris-carbonato complex of uranium ($UO_2(CO_3)_3^{4-}$) with an immobilized derivative of ethylenediamine as reported by Jablonski and Leyden.[3] The silica-cellulose filter is chemically modified by silylation with a silane-ethylenediamine. This method combines the advantages of a one-step filter pretreatment, a single step UO_2^{2+} extraction and enrichment onto a solid substrate and the simplicity of an x-ray fluorescence determination.

EXPERIMENTAL

Reagents and materials

N-β-ethyl-γ-aminopropyl trimethoxysilane (Dow–Corning Z-6020) was was used as a 10% v/v solution in toluene. The filters (22 or 25 mm diameter) were punched from sheets of SG-81 (Whatman, Inc.), 20% w/w silica gel in cellulose after silylation. Stock solutions were prepared from reagent grade chemicals, copper from the chloride salt as a 1000 mgL^{-1} aqueous solution and uranium from uranyl acetate as a 5000 mgL^{-1} solution. Working standards were subsequently prepared from these solutions as needed. Samples from various stages in the uranium solution mining process were obtained from Wyoming Minerals, Inc. These samples represented a range of uranium concentrations in a varying matrix, although all samples were aqueous solutions.

Apparatus

The flow system used for uranium extraction and enrichment is the same as described earlier[2] with the exception that a 25 mm diameter filter is used. The XRF spectrometer is a Philips PW 1410/60 equipped with a molybdenum tube, a LiF-200 crystal and a NaI scintillation counter. The following operating conditions were used for the uranium determinations: Mo x-ray tube operated at 90 kV and either 12 or 34 mA depending upon the range of concentrations studied, sample rotation (60 rpm) with 100 s counting time and fine collimation. The angles used for the uranium determination were the $U_{L\alpha}$ at 26.14° 2θ and background at 25.5° 2θ and 27.2° 2θ.

Procedure

The SG-81 filters are chemically modified by silylation using the 10% v/v Z-6020 solution in toluene following the procedure previously reported.[4] The filters were stored in a cool, dark, dry place after silylation and no deterioration was noted over a period of several months. Chemical capacity of the filters was determined by passing 100 mL of the 1000 ppm Cu^{2+} stock solution through the silylated filter at a flow rate of 5 mL/min followed by 10 mL of deionized water. After drying Cu^{2+} was eluted from the filter using 30 ml of 30% v/v hydrochloric acid in deionized water. The copper concentration in the eluent was determined by atomic absorption using standard procedures.[4,5]

The relative amount of Cu^{2+} extracted by the silylated filters at various pH values was determined using 50 mL of 2 ppm Cu^{2+} solution, adjusted to constant ionic strength ($\mu=0.5$) with $NaClO_4$.[6] The pH of the solutions was adjusted using either 0.1 N HCl or 0.1 N NaOH. The final pH was determined using a Corning pH meter (model 109) with a combination pH electrode. The relative concentration of Cu^{2+} on the filters at the various pH values was determined as in the chemical capacity study.

Uranium enrichment on the silylated filter involves the ion-pairing of $UO_2(CO_3)_3^{4-}$ with the immobilized ethylenediamine between pH 6 and 8. Thus the uranium working standards and the process samples were prepared as follows: the required aliquot of either the stock solution or process sample was pipetted into a volumetric flask and brought to volume so that the sample used for enrichment would be 0.1 M in $(NH_4)_2CO_3$ and at a $pH=6.5\pm0.2$. In the case of the process samples, the aliquot was first pretreated by acidifying to pH 2 and heating to just boiling followed by cooling and neutralization. The pretreatment is required to remove any carbonate that might be present.[3]

The procedure for uranium extraction is the same as in (2) except a 25 mL sample and a cycling time of 60 min is used. This is followed by washing the filter with three 5 mL portions of 0.1 M $(NH_4)_2CO_3$ solution ($pH=6.5$). The filter is then prepared for XRF analysis by air drying and placing it in a 25 mm diameter sample holder (Chemplex) between two sheets of 6.3 μm thick Mylar film.

RESULTS AND DISCUSSION

The performance of the SG-81 filters silylated with Z-6020 as preconcentration tools was compared to the performance of bulk silica gel silylated with Z-6020 by determining the chemical capacity of the filters for Cu^{2+} and the relative extraction of Cu^{2+} per filter; a 22 mm diameter filter weighs 45 mg ± 1 mg. Allowing for the 20% by weight silica in the filter, this calculates to be a capacity of 1 mmole/g of silica which agrees with that reported for bulk silica gel.[4] The results of the relative extraction of Cu^{2+} versus pH on SG-81 is plotted in Figure 1; also plotted are the results of the same experiment using bulk silica gel.[4] The main point of Figure 1 is to show that the extraction of Cu^{2+} on SG-81 has approximately the same pH dependence as on the bulk silica gel. It was concluded that the immobilized ethylenediamine on the SG-81 filters was similar to the ethylenediamine immobilized on bulk silica gel. In addition, even though the capacity of each filter is low, their convenient physical form makes the filters attractive as preconcentration tools in XRF analysis.

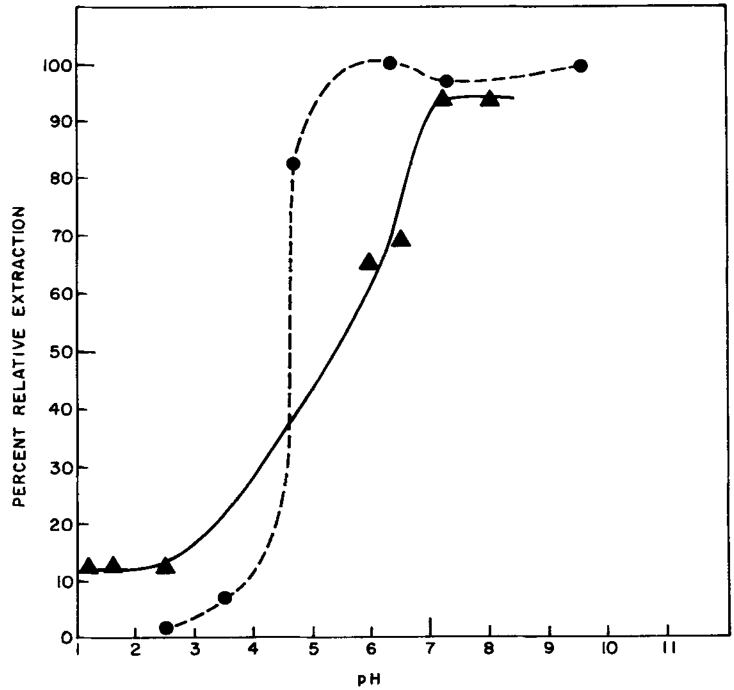

FIGURE 1 Percent relative extraction of copper onto chemically-modified silica gel (- - -●- - -) and SG-81 filters (——▲——) versus pH.

The time needed for optimum uranium enrichment on the filter was determined by cycling 25 mL of a 2 ppm U solution for various times through the flow system at a rate of 30 mL/min, followed by XRF analysis of the filters for uranium. The data is shown in Figure 2 as x-ray counts of the $U_{L\alpha}$ line versus cycling time in minutes. The datum at 1.5 minutes

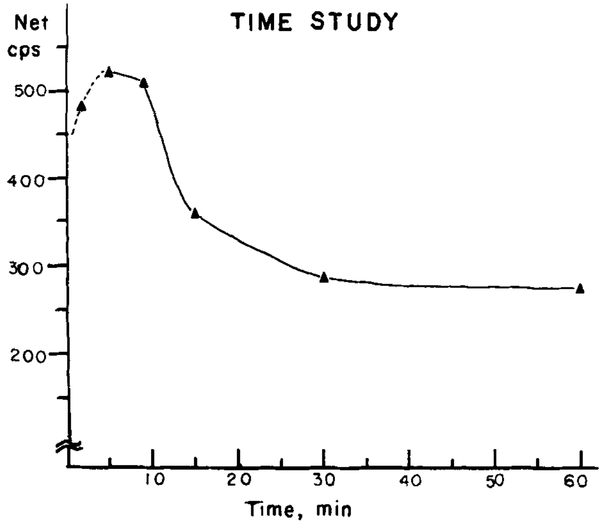

FIGURE 2 Effect of cycling time on recovery of uranium on chemically-modified SG-81 filters.

represents one volume of sample solution passed once through the filter and into waste; the other data points represent cycling of the sample. The cycling time needed for maximum enrichment occurs at the time of maximum x-ray signal; however, precision is poor at short times (≤ 30 min.). As the cycling time is increased a steady state value of cps versus time is reached and the precision of the method increases. Thus a 60 minute cycling time was chosen for enrichment and extraction.

Two experiments were done to determine the suitability of the filters for XRF analysis. The first study dealt with determining the necessity of counting both sides of the filter in the XRF spectrometer. A series of solutions of various uranium concentrations was preconcentrated by this method followed by x-ray counting of the $U_{L\alpha}$ line on both sides of the filters. A plot of cps of the contact side of the filters (the side facing the sample solution) versus cps of the average of the front and back counts of the filter was constructed and a straight line was obtained with a slope of 0.96 ± 0.03 and a correlation coefficient of 0.9991. This indicates that counting of only one side of the filter is sufficient for the uranium determination. In the second experiment pressing of the filters to improve the precision of the counting statistics was investigated. A series of filters containing varying amounts of uranium was first measured by XRF followed by pressing at 10,000 psi for 20 s in a one inch die and remeasured. Using two-group statistics, no significant difference at the

95% confidence level was observed between the XRF signals from the unpressed and pressed filters.

Two methods were used to determine the percent recovery of uranium of the filters. In the first method, two filters were used in succession; a sample was preconcentrated onto one filter, the filter was removed and a second filter was used to concentrate the uranium remaining in the sample. The second method involved a comparison of the x-ray counts of a sample filter with another filter spiked with a known amount of uranium. Mean recovery ranges from 70 to 95% for 10 ppm (in a 25 mL sample).

A calibration curve was constructed in the range of 0 to 250 μg U using a 25 mL sample volume. The curve is shown in Figure 3. The slope of the regression line is 6.4 ± 0.1 (RSD = 1.4%) and the correlation coefficient is 0.9981 with a Student's *t* of 73.80 (21 points). The precision of the method was calculated from the x-ray intensities of the $U_{L\alpha}$ line at 125 μg (10 replicates) and 12.5 μg U (3 replicates); at the 95% confidence level the relative standard deviation is found to be 3.7% and 3.2%, respectively. The lower limit of detection for a 100 s. counting time was calculated from

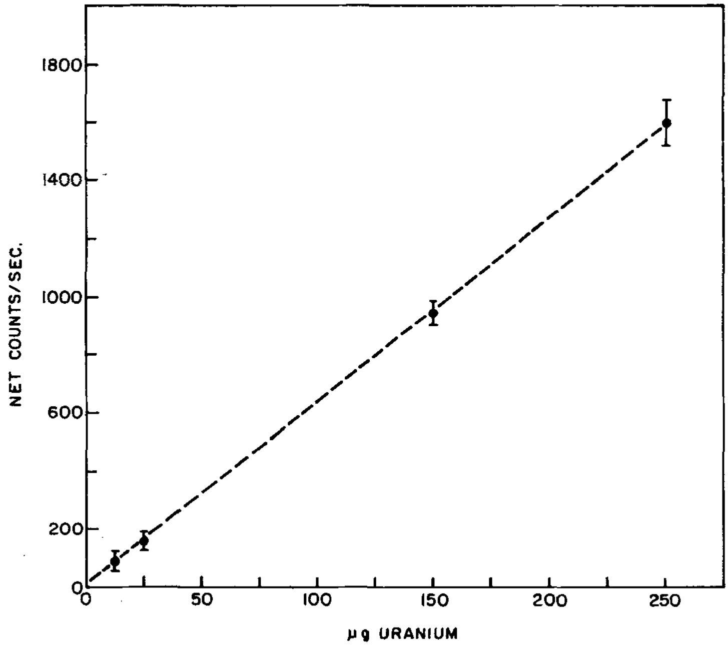

FIGURE 3 X-ray intensities versus micrograms of uranium on chemically-modified SG-81 filters.

TABLE I

Data from industrial process samples

Industrial process samples	Process lab, conc., ppm U	$Ba_2UO_2(CO_3)_3$/ x-ray ppm U	PAR/Colorimetry ppm U	This method	
				ppm U	RSD, %
1 (6×)	38.8	—	—	34.6	3.02
2 (3×)	1.06	0.86	0.95	0.99	4.2
3 (5×)	1.5	1.09	1.20	1.03	8.1

the Y-intercept of the calibration curve (Y-intercept $= -5.0 \pm 12$). At the 99% confidence the LLD is 5.4 μg U or 220 ppb in a 25 mL sample volume.

The solution mining process samples were then analyzed for uranium using this method and the results are presented in Table I. At the 95% confidence level there is no significant difference between the uranium concentration determined by this method and the uranium concentration as reported by the process laboratory. For two samples the results of this method also agree with two other independent analytical methods for uranium.[7,8]

SUMMARY

This study presents a method for the extraction and enrichment of UO_2^{2+} from aqueous solutions. Sample preparation for subsequent x-ray fluorescence analysis can be done in a single step using SG-81 filters chemically-modified with Z-6020. The determinations can be made with a precision of 96% with a detection limit of 5.4 μg U in a 25 mL sample volume.

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