Uranium Determination in Water, Soil and Stone Through Adsorptive Accumulation of U(VI)-chloranilic Acid Complex

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Abstract

Uranium concentrations in water, soil and stones collected from six different locations of Sherpur District, Bangladesh, were determined by adsorptive cathodic stripping (ACS) voltammetric technique. The technique is based on the adsorptive accumulation of the uranium(VI)-chloranilic acid (CA) complex onto a hanging mercury drop electrode, followed by reduction of the complex by cathodic voltammetric scan using differential pulse modulation. The set optimum experimental conditions were of pH value 2.5, CA concentration ~ 1.95 x 10^{-4} M, deposition potential + 90 mV, deposition time 120 s, scanned potential ranges – 35 mV to – 150 mV, pulse amplitude 25 mV and scan rate 2 mV/s. Solution of 0.02M KNO_3 was used as electrolyte and EDTA of concentration ~ 1.95 x 10^{-5} M was used to reduce the interferences of unwanted metal ions. 200 µl and 100 µl volumes of soil and stone digested samples in the investigation cell downed to 52- and 103-fold dilutions facilitated to determine uranium concentrations in trace element levels. The concentrations were found in ppb level. For example, 3.8 and 5.3 ppb values were obtained for a soil and a stone sample, respectively. For a water sample, 10.3 ppb value was obtained. The range of the calculated values of uranium concentrations in water, soil and stones were found to be 8.9-16.4 ppb, 16.3-31.7 ppm and 19.2-161.6 ppm, respectively.

Keywords: Uranium, water, soil, sand, stone, U(VI)-CA complex, adsorptive accumulation.

1. Introduction

Uranium is a naturally occurring radioactive element that exists in the form of isotopes with the quantity of U^{238} (99.27%), U^{235} (0.72%) and U^{234} (0.01%). The sources of uranium are generally rock, stone, soil, sand and water. A great amount of uranium is extracting from its source mine every year. It has been used industrially as a nuclear fuel for more than fifty years and has a great potential to be used for many years in the future. World reactor related uranium demands are projected to be as high as 122000 tons by 2035 [1]. Thus, uranium is considered to be one of the significant commercial items of the world energy market. However, as a deadly toxic element its exploration, extraction and utilization involve sophisticated technologies and techniques.

Air, soil, vegetations, aquatic media and the ecosystem can be contaminated by the uranium released from different sources. The effluent of nuclear industries, nuclear waste disposal sites, leached uranium from uranium rich matrices, dispersed uranium from the mining and processing sites, nuclear accident and lastly from the egoistic blasting of nuclear weapons and dirty bombs can be considered as the main sources of uranium contamination. Human body being contaminated by uranium severely suffers from uranium toxicity [2]. Ingestion, i.e., eating and drinking stuffs, is considered to be the main route among other ways of uranium intake by human. Thus, monitoring of uranium up to trace level is very important. Conversely, extraction of uranium for industrial application, obviously with maximum caution, is indispensable too. Therefore, extensive researches are being carried out worldwide on the environmental monitoring and concurrently searching deposits of uranium in its probable media for extraction [1].

It has been known that some areas of Bangladesh are moderately rich in uranium. A number of drives have also been given to quantify uranium in different matrices of different locations of Bangladesh [3-5]. It is well documented that India has a big uranium deposit at its West Khasi Hills in Meghalaya District which is adjacent to the northern part of Bangladesh. Almost alike geological structure of the northern part of Bangladesh with that of Meghalaya District, provides good indication of having uranium deposits at the northern areas of Bangladesh. With a view to find out the facts and concurrently to achieve a database, and also keeping in mind the high commercial values of uranium, plan has been taken to search uranium in different locations of Bangladesh as well as to quantify uranium concentrations in different matrices such as water, beach sand, soil, rock and stones [4, 5].

Uranium can be determined through various techniques. But, determination of uranium in trace level by electrochemical means is an innovative technology. High sensitive voltammetric techniques such as various forms of stripping voltammetry are reported to be able to quantify uranium with relatively simple and less expensive way [6, 7]. Among stripping voltammetry, the adsorptive stripping voltammetry (ASV) is reported to be a powerful technique for trace uranium analysis [7]. In this technique, uranium is pre-concentrated on to the surface of a fresh mercury drop at a fixed potential by adsoroption and then it is allowed for measurements between the chosen potential regions through decomposition. To minimize the bad impact of other

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electroactive species, when they are remarkably present in the sample, and concurrently to enhance the efficiency of the technique, nowadays various complex forming organic ligands are utilized too. Among them catechol [8], oxine and cupferron [9], aluminon [10], pyromellitic acid [11], thioglycolic acid [12] and chloranilic acid (CA) [5, 13-17] are extensively investigated. In case of CA, at an optimum experimental condition, its adsorption range of potential onto a mercury drop and the mechanism of formation of U(VI)-CA complex are almost clear [5, 13, 17]. The limiting concentration of uranium to be determined by using CA is also anticipated [5, 17]. These valuable findings and information enable one to apply its relatively selective accumulation at potentials where usual nonionic organic contaminants and all other metal-CA complexes are hardly adsorbed [5, 17].

The present study attempts to determine uranium in water, soil and stones of different locations of the Sherpur District, Bangladesh. This district is situated near the border of India and not too far from the uranium deposit of West Khasi Hills present in the Meghalaya District of India. Almost alike geological formation of Meghalaya and Sherpur may be a fact of having uranium deposits in this part of Bangladesh. The chosen method is the cathodic adsorptive stripping voltammetry (CASV) which seems to be a user friendly technology for trace uranium determination in such matrices.

2. Materials and Method

2.1 Sampling location and sample collection

Fig. 1 shows the sampling locations are Poragaon, Kakrakandi, Bheula, Garjaripa, Jhenaigati and Dhansail, as marked by circles, which situated in the north part of Sherpur District, Bangladesh. Water, soil and stone samples were collected from these places.

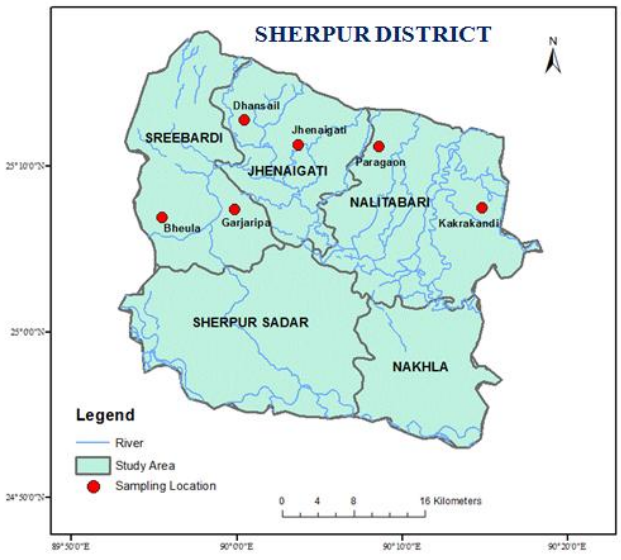

Fig. 1 Sampling locations: Kakrakandi, Garjaripa, Bheula, Poragaon, Jhenaigati and Dhansail (marked by circles) of Sherpur District, Bangladesh

Water samples included surface and underground water were collected in acid washed polythene bottles. Each sample (~ 500ml) was immediately acidified by adding 100 µl of 1M HNO_3. Soil samples were collected from around one feet depth of surface. Stone samples were collected from the earth surface of hilly areas. Both the soil and stone samples were collected in clean polythene bags with adequate precautions.

2.2 Chemicals

All the chemicals used were of analytical reagent grade and/or suprapur. Distilled water was used to prepare the reagent solutions and for rinsing the glass wares and the three-electrode cell system. 1000 ppm uranium standard solution acidified with 1M HNO_3 of volume 100 ml was prepared by dissolving Uranyl Nitrate $[UO_2(NO_3)_2.6H_2O]$ (May and Baker Ltd., Dagenham, England). 100 ml 0.01M Chloranilic acid (CA) (Alpha Aesar, USA) solution, 100 ml 0.01M EDTA solution (Merck, India), 250 ml 0.2M KNO_3 solution (Merck, India), 100 ml 1M HNO_3 (Merck, India), 250 ml 5M HNO_3, 250 ml 2M HF (BDH), 250 ml 2M $HClO_4$ (Merck, India) and 100 ml 1M NaOH (BDH) were duly prepared.

2.3 Sample preparation

2.3.1 Water sample preparation

For the adsorption accumulation studies of uranium, each water sample was made ready by filtering through filter paper of porosity 0.45 µm. It was done to separate any plotting and particulate materials. Then the pH value was adjusted to 2.5 by adding 1M HNO_3 drop wise.

2.3.2 Soil sample preparation

Each soil sample was oven dried to a constant weight at 333 K. Then about 1.0 g of soil was taken into a perfluoroalkoxy polymer container and reacted with 2 ml 2M HF and 3 ml 5M HNO_3 for a 12 h. After then, the container with the generated mass was placed in a microwave pressure vessel. There 10 ml 5M HNO_3:2M $HClO_4$ (4:1v/v) was added with it and digested at 180°C for 10 minutes. After cooling, the produced solution was filtered through a 0.45 µM syringe and diluted to 100 ml by adding water. But, before adjusting this volume, pH value of the solution was adjusted to 2.5 by adding 1M NaOH drop wise and stirring.

2.3.3 Stone sample preparation

Each stone sample as collected was crushed and then grinded to powder in a PTFE mortar. Powder was then oven dried at 333 K to a constant weight. After that, around 0.5 g powder was subjected to acid treatment and successively followed microwave digestion. The procedure was identical to that applied for soil sample as described in the sub-section 2.3.2. The sample volume and sample pH were kept to 100 ml and 2.5, respectively.

2.4 Apparatus

Uranium concentration determination was carried out by using Princeton Applied Research (PAR) model 174A polarographic analyzer. PAR 303 hanging mercury drop

electrode (HMDE) was used as the working electrode, i.e., electrode for adsorption and desorption of uranium, Ag/AgCl as the reference electrode and a platinum wire as the counter electrode. An XY recorder of model RE0089 was used for sketching the voltammograms [current *(i)* vs. potential relationships *(c)*] of the reduction of U(VI)-CA complex. A magnetic stirrer of Model 305 was used for the mixing of the sample and added uranium standard with the electrolyte solutions in the cell sample cup. A Metrohom 692 digital pH meter was used for the pH measurement.

2.5 Analytical Procedure

2.5.1 Understanding the feature of U(VI)-CA complex reduction peak current (i) vs. uranium concentration (c) for blank solution and uranium standards

At first 25 ml 0.02 M KNO_3 electrolyte solution was prepared from 0.2 M KNO_3 solution by dilution. Then 0.5 ml CA and 50 µl EDTA solutions were added with it and mixed. The pH value of this mixture was adjusted to 2.5 by adding 1M HNO_3 drop wise and stirring. As a result, a mixture of volume around 25.6 ml became ready. In the mixture, the concentrations of CA and EDTA downed to 1.95×10^{-4} M and 1.95×10^{-5} M, respectively. Then 10 ml mixture was pipetted into the cell cup and set it to the three-electrode cell system of the voltammetric analyzer. The mixture was then deaerated with nitrogen for 10 minutes under stirring. The stirrer was then switched off and for stripping analysis deposition potential was set to + 90 mV. After then on a fresh mercury drop, the accumulation of CA, and concurrently U(VI)-CA complex if any trace uranium is present in the mixture, was continued for 120 s under stirring condition. Following the accumulation step, stirring was stopped and after a quiescent period of 30 s a negative potential scan i.e., cathodic stripping was made using differential pulse modulation at a scan rate of 2 mV/s with pulse amplitude of 25 mV in the scanning potential range from-35 mV to-150 mV. As a result, a voltammogram (current vs. potential curve) for the blank mixture is obtained through the XY recorder. Then 10 µl uranium standard solution of concentration 10 ppm was added to the cell cup. This standard was made from 1000 ppm uranium standard solution by dilution. So, the uranium standard addition became to 10 ppb. The mixture was then stirred for 5 minutes and stopped. Thereafter, successively setting up the deposition potential, by producing a fresh mercury drop, completing of accumulation, setting up scanning potential range and starting scanning a voltammogram for the U(VI)-CA complex reduction peak current *(i)* vs. uranium concentration *(c)* for the first standard addition was obtained. In such a way five consecutive uranium standard additions (10, 20, 30, 40 and 50 ppb) were carried out with a view to obtain *i vs. c* feature of U(VI)-CA complex.

2.5.2 Behavior of U(VI)-CA complex reduction peak current (i) vs. uranium concentration (c) for the water samples

In case of water samples, 10 ml water was pipetted into the cell cup and set it to the three-electrode cell system of the voltammetric analyzer. After then 0.2 ml CA and 20 µl EDTA solutions were added with it. After that all the successive steps starting from deaeriation to sketching voltammogram as carried out for the blank solution were followed and the U(VI)-CA reduction peak for the unknown uranium present in the water sample was obtained. Thereafter, uranium standard addition was continued for three times (10 ppb, 15 ppb and 20 ppb). From the *i vs. c* relationships of the U(VI)-CA reduction peaks, the amount of uranium present in the water in ppb level was obtained. Using this value, uranium contained in 10.22 ml mixture present in the cell cup, at the zero addition level, was found out. This amount of uranium is the uranium present in the 10 ml water sample. From it uranium present per liter water was calculated.

2.5.3 Behavior of U(VI)-CA complex reduction peak current (i) vs. uranium concentration (c) for soil samples

In case of soil samples, 10 ml 0.02 M KNO_3 electrolyte solution of pH 2.5 was taken in the cell cup and set to the cell of the analyzer. Then 0.2 ml CA, 20 µl EDTA and 200 µl soil sample solutions were added with it. After that by adopting earlier procedure, voltammograms of U(VI)-CA reduction peak for the unknown uranium and three successive uranium standard additions (10 ppb, 20 ppb and 30 ppb) were obtained. The *i vs. c* relationships of the U(VI)-CA reduction peaks cleared about the amount of uranium present in the added sample in ppb level. Using this value, uranium contained in 10.42 ml solution present in the cell cup, at the zero addition level, was found out. This amount of uranium is the uranium present in the 200 µl soil sample. From this value uranium present in 100 ml sample was calculated. This amount of uranium is present in the digested amount of soil. Using this value, the amount of uranium present per Kg soil was obtained.

2.5.4 Behavior of U(VI)-CA complex reduction peak current (i) vs. uranium concentration (c) for stone samples

In case of stone samples, 10 ml 0.02 M KNO_3 electrolyte solution of pH 2.5 was taken in the cell cup and set to the cell of the analyzer. Then 0.2 ml CA, 20 µl EDTA and 100 µl stone sample solutions were added with it. Voltammograms for the unknown sample and three successive uranium standard additions (10 ppb, 20 ppb and 30 ppb) were sketched. From the *i vs. c* relationships of the U(VI)-CA reduction peaks, the amount of uranium in ppb level was obtained. Using this value uranium contained in 10.32 ml solution present in the cell cup, at the zero addition level, was found out. This amount of uranium is the uranium present in the 100 µl stone digested solution. By using this value, the amount of uranium present in the digested amount of stone and then uranium present per Kg stone was obtained.

3. Results and Discussion

Fig. 2 shows the adsorptive cathodic stripping (ACS) voltammograms obtained for the U(VI)-CA complex reduction at different uranium concentrations. It can be seen that a well defined U(VI)-CA complex reduction peak is

appeared in between the potential range of – 55 mV to – 125 mV. Reduction peak current value *(i)* gradually increased with increasing the concentrations of uranium *(c)*. The inset Fig. 2(a) shows the *i vs. c* relationships of the U(VI)-CA complex reduction. It can be seen that the relationships show linearity up to 42 ppb added uranium with R^2 value of 0.996 beyond which a clear non-linearity is appeared. This is a long linearity range and seems will allow the method to be used to measure unknown sample having appreciable amount of uranium in trace level.

Linearity up to 30 ppb uranium with R^2 value of 0.99 and up to 50 ppb uranium with R^2 value of 0.89 was reported by the authors [15]. The method was used to quantify uranium in the lichen sample. Nevertheless, present study informs that 42 ppb is the limiting uranium concentration to be present in the investigated solution to avoid experimental inaccuracy. This value is equal to the value of the total uranium present in an unknown sample plus added uranium standard. The inset Fig. 2(b) shows the enlarge version of the fraction of the (i) vs. (potential, mV) relationships obtained for the blank solution. The appearance of a very small peak hump is indicating that the used water, electrolyte, reagents and ligands are almost free from uranium contamination. It is signifying that without any major interruption effect, the mixture of the set electrolyte, reagents and ligands to be applied to quantify uranium concentrations in the targeted samples in trace level.

Fig. 3 shows the ACS voltammograms of the U(VI)-CA complex for a water sample with 10 ppb, 15 ppb and 20 ppb uranium standard additions. It may be seen that a smooth and a well defined voltammogram with a reduction peak is appeared for the water sample. The peak appeared at the potential of – 90 mV as that obtained for the reduction peak of uranium(VI)-CA complex when 10 ppb uranium standard was added in the mixture solution as shown in Figure 2. It indicates that the water sample consists of uranium.

The inset Fig. 3 shows the *i vs. c* relationships of the U(VI)-CA complex reduction. It may be seen that *i vs. c* shows a linear relationship which passes through the *i* line (Y-axis) and touches the *c* line (X-axis) at the concentration of 10.3 ppb. It means that 10 ml water sample consists of 105.27 ng uranium (solution volume in the cell cup was 10.22 ml). Therefore, 10.53 μg of uranium is present in one liter of water. In such a way, uranium concentrations in 36 water samples were determined. The obtained uranium concentration values are presented in the Table 1. It may be seen that the values lies in between 8.9-16.4 ppb. For drinking water, the permissible intake level of uranium is very low. As for example, United States Environmental Protection Agency (EPA) suggests maximum uranium contaminant level of 30 ppb [18] and the World Health Organization (WHO) harshly recommended the level of 15 ppb only [19]. At around 20% cases, the presently obtained values are higher than the recommended value of WHO [19]. The peoples living in this area are directly drinking this water and using it for their cooking and daily works. It seems that uranium concentrations in water of those areas are not so alarming yet.

Fig. 4 shows the ACS voltammograms of the U(VI)-CA complex for a soil digested sample of volume 200 μl with 10 ppb, 20 ppb and 30 ppb uranium standard additions. The amount of soil sample taken for the microwave digestions is listed in the Table 1. It is notable that the amounts were fixed up by carrying out a series of ACS analysis on the reduction behavior of the U(VI)-CA complex. It can be seen that a smooth and a well defined voltammogram with a reduction peak is appeared for the sample. The appearance of such a smooth peak is obviously the positive effect of appropriate dilution of the sample (1:52 fold) and the use of masking agent EDTA. However, the appearance of the U(VI)-CA reduction peak informs that the added soil digested sample consists of uranium. With increasing uranium concentration, increase in peak current behavior is analogous to that observed for the blank sample (Fig. 2) and water sample (Fig. 3).

The inset Fig. 4 shows the *i vs. c* relationships of the U(VI)-CA complex. The linear line of the *i vs. c* touches the uranium concentration line (X-axis) at the concentration of 3.8 ppb. It means that 200 μl soil digested sample consists of 39.59 ng uranium (volume in the cell cup is 10.42 ml). Amount of uranium in 100 ml prepared sample is 19.79 μg. This amount of uranium is present in 0.9016 g of soil which corresponds to 21.95 mg uranium/Kg soil i.e. 21.96 ppm uranium in the soil. Table 1 summarizes the uranium content found in the soil samples collected from different locations. It may be seen that the obtained values lie in between 16.3-31.7 ppm. At around 5% cases, the presently obtained values are higher than 30 ppm. Actually, there are no guidelines of EPA or WHO for the safe level of uranium in soil as that provided for water. Canadian Council of Ministers of the Environment (CCME) has a published guideline on the safe level of uranium in soil [20]. According to this guide line, it seems that uranium concentrations present in the soils of the investigated areas are not so alarming.

Table 1: Data for the amount of digested soils and stones, volumes of sample prepared, volumes of sample taken and added and the concentrations of uranium obtained in water, soil and stones collected from the different locations of Sherpur District, Bangladesh

Sample name	Number of samples studied	Weight of digested sample (g)	Sample volume made (ml)	Added sample volume (μl)	Uranium concentration μg/L (ppb)	Uranium concentration mg/Kg (ppm)
Water	36	-	25.0	10×10^3	8.9 - 16.4	-
Soil	30	0.9016 - 1.0013	100	200	-	16.3 - 31.7
Stone	30	0.5026 - 0.5221	100	100	-	19.2 - 161.6

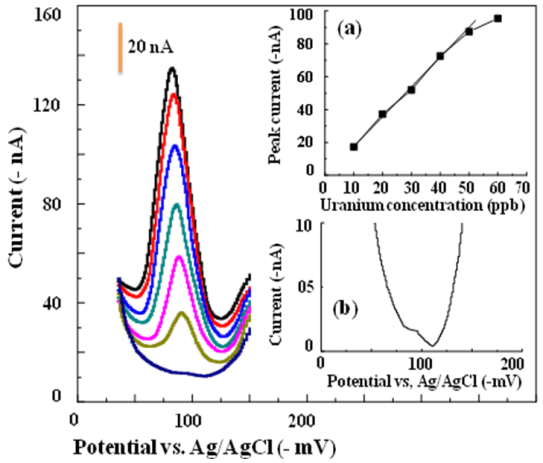

Fig. 2. ACS voltammograms of the U(VI)-CA reduction during uranium standard additions (0, 10, 20, 30, 40, 50 and 60 ppb) [pH 2.5, 0.02 M KNO_3 electrolyte, 1.95 x 10^{-4} M CA and 1.95 x 10^{-5} M EDTA]. Inset Figures: (a) U(VI)-CA reduction peak current (i) and uranium concentration (c) relationships and (b) (i) vs. (potential) relationships for the blank solution

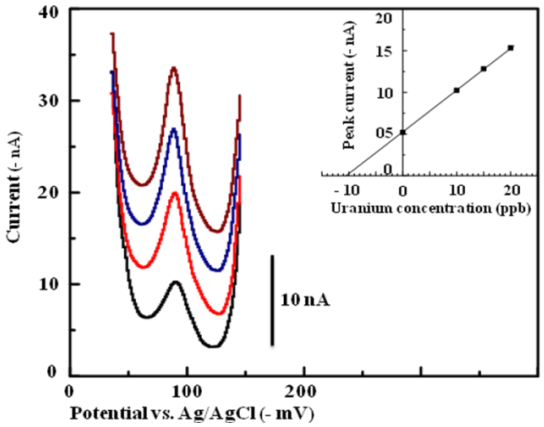

Fig. 3 ACS voltammograms of the U(VI)-CA reduction for a water sample with 10, 15 and 20 ppb uranium standard additions [pH 2.5, 0.02 M KNO_3 electrolyte, 1.96 x 10^{-4} M CA and 1.96 x 10^{-5} M EDTA]. Inset Fig.: Relationships between the U(VI)-CA reduction peak current (i) and concentration of uranium (c)

Fig. 5 shows the ACS voltammograms of the U(VI)-CA complex for 100 µl stone digested sample with three successive uranium standard addition (10, 20 and 30 ppb). The amounts of stone powder taken for the microwave digestions are enclosed in the Table 1. These amounts were fixed up by carrying out a series of ACS analysis on the reduction behavior of the U(VI)-CA complex. The purpose of series of analysis was to optimize the least volume of digested sample need to be added to 10 ml mixture of electrolyte and ligand to obtain around 10 ppb uranium concentration i.e. trace level uranium. The second purpose was to minimize as possible as the unwanted effect of other metal ions present in the sample on the desired U(VI)-CA complex. It was observed that the optimized condition (pH 2.5, CA concentration 1.95 x 10^{-4} M and EDTA of concentration 1.95 x 10^{-5} M) was enabled in suppressing the side effect of foreign materials on the U(VI)-CA complex. Such a benefit was also achieved by the authors [8, 9] to inactivate unwanted metal ions such as Cu(II), Fe(III), Mn(II), Zn(II) and Pb(II) present in digested sample.

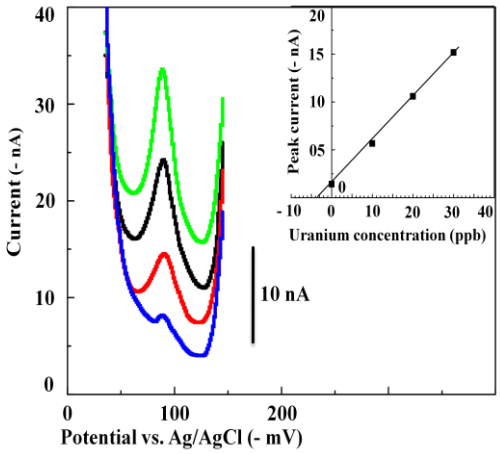

Fig. 4 ACS voltammograms of the U(VI)-CA reduction for a soil sample with 10, 20 and 30 ppb uranium standard additions [pH 2.5, 0.02 M KNO_3 electrolyte, 1.92 x 10^{-4} M CA and 1.92 x 10^{-5} M EDTA]. Inset Fig.: Relationships between the U(VI)-CA reduction peak current (i) and concentration of uranium (c)

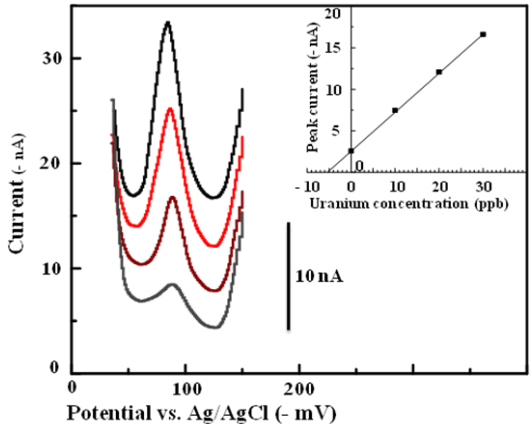

Fig. 5 ACS voltammograms of the U(VI)-CA reduction for a stone digested sample with three successive uranium standard additions (10, 20 and 30 ppb) [pH 2.5, 0.02M KNO_3 electrolyte, 1.94 x 10^{-4} M CA and 1.94 x 10^{-5} M EDTA]. Inset Fig.: Relationships between the U(VI)-CA reduction peak current (i) and concentration of uranium (c)

From the Fig. 5, it can be seen that a well defined voltammogram with a reduction peak is appeared for the unknown stone digested sample. The appearance of smooth peak is obviously the positive effect of appropriate dilution (1:103 fold) of the digested sample solution and the use of EDTA [8, 9]. The peak appeared at the potential of – 89 mV which can be taken equal to the potential – 90 mV obtained for the reduction peak of uranium(VI)-CA complex when 10 ppb uranium standard was added with the blank solution as shown in Fig. 2. It may be taken as an indication that the stone digested sample consists of uranium.

The inset Fig. 5 shows the *i vs. c* relationships of the U(VI)-CA complex. Linear line of the *i vs. c* touches the uranium concentration axis (X-axis) at the concentration of 5.3 ppb. It means that 100 μl stone digested sample consists of 54.69 ng uranium (volume in the cell cup is 10.32 ml). So, amount of uranium in 100 ml prepared sample is 54.69 μg. This amount of uranium is present in 0.5221 g of stone which corresponds to 104.75 mg uranium/Kg stone i.e. 104.75 ppm.

Table 1 summarizes the uranium content found in the stone samples collected from different locations. It may be seen that the obtained values lie in between 19.2 - 161.6 ppm. At around 9% cases, the presently obtained values are higher than 150 ppm. Although, this concentration is not economically viable to extract uranium from these stones but it requires an extensive study to find out the uranium crust layer if any to understand the leaching property and to estimate uranium abundances. It is noteworthy to mention here that the long-term retention of the high content of uranium as observed in the soil and stone of some investigated areas may experience a radiation risk in the human health living in those areas in near future [2]. Therefore, monitoring, i.e., uranium quantification, radiation dose estimation and activity regarding radioactive remediation seems to be essential.

4. Conclusion

The present study demonstrates that CAS voltammetric determination of uranium based on accumulation of the U(VI)-CA complex can be used to quantify uranium concentrations in water, soil and uranium rich stones by measuring uranium in trace level as selected. It seems that the adopted experimental optimum conditions are quite suitable to minimize the interferences of other metal-ions present in water and especially soil and stones during uranium determination. The method is not complex and highly selective. Success of this study seems to be opened a new scope to enhance the uranium exploration and quantification studies at various geographical locations of Bangladesh. However, more investigations are needed to be carried out because soil and stones of different locations of Bangladesh may contain different elemental compositions and may impart different complexities in the measurements.

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