Determination of uranium in stream water, beach sand and rocks by stripping voltammetry following adsorptive accumulation of the U(VI)-chloranilic acid complex

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Abstract -*An attempt has been taken to determine the uranium contents in the water of a stream branch, beach sands and uranium rich rocks collected from different locations of Bangladesh, by adopting trace uranium determination technique. The technique is based on the adsorptive accumulation of the uranium(VI)-chloranilic acid (CAA) complex onto a hanging mercury drop electrode, followed by reduction of the complex by cathodicvoltammetric scan using differential pulse modulation. The experimental optimum conditions were pH value 2.5, CAA concentration 1.95×10^{-4} M, deposition potential + 90 mV, deposition time 120 s, scanned potential ranges of – 35 mV to – 150 mV, pulse amplitude 25 mV and scan rate of 2 mV/s. 0.02M KNO_3 solution was used as electrolyte and EDTA solution of concentration 1.95×10^{-5} M was used in view to turning down the interferences of unwanted metal ions present in water, and sand and rock digested samples. The U(VI)-CAA complex reduction peak current vs. added uranium concentration showed a linearity up to 43 ppb with a limit of detection of 0.316 ppb. 5.0 ml stream water sample, and 200 μl and 100 μl volumes of sand and rock digested samples in the investigation cell downed to 2, 52 and 103 fold dilutions facilitated to determine unknown uranium concentrations in trace element levels. The unknown concentrations found in ppb level and were in between 3.6 to 9.8 ppb. On calculation, uranium concentration in stream water, beach sands and rocks were found to be 21 ppb, 34.42-39.55 ppm, and 530.08 and 108.89 ppm, respectively. The present work seems to be the first investigation on the quantification of uranium in high uranium containing rocks through trace level determination technique 'differential pulse cathodic stripping voltammetry (DPCSV)'.*

*Keywords:*Uranium, stream water,sand, rock, U(VI)-CAA complex, adsorptive accumulation, DPCSV, EDTA.

1. INTRODUCTION

Uranium is a naturally occurring radioactive element and 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. It is recorded that uranium has been using industrially as a nuclear fuel for more than fifty years and seems to be used up to far future. In 2012, a total of 437 commercial nuclear reactors consumed about 61980 tons of uranium. World reactor related uranium requirements are projected to be rise to 122000 tons by 2035 [1]. Therefore, nowadays, uranium is considered to be one of the crucial industrial fuels and concurrently a profitable business item to hiking the economy of a country. But, the narrative is not a state forward work because uranium in parallel is a deadly toxic element.

Air, soil, vegetations, aquatic media, i.e. the environment and the ecosystem can be contaminated by the uranium released from different sources. The main sources can be exemplified as the effluent of various 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. Human

body when contaminated by uranium is severely suffers from the uranium toxicity [2]. Although intake of uranium by human may take place through various ways, the prime route of ingestion may beconsidered to be through the drinking stuffs. 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[3] and World Health Organization (WHO) harshly recommended the level of 15 ppb only [4].So, environmental monitoring of uranium up to trace level is very important. On the other hand, extraction of more uraniumfor industrial application, obviously with maximum caution, is indispensable too. Therefore, worldwide peoples have been extensively carrying out research on the environmental monitoring and concurrently broadly searchingdeposits of uranium in its probable mediums for extraction [1].

Bangladesh highly needs the exploration of uranium for its future nuclear power industry. Besides it, fuel material for the existing TRIGA MARK-II research reactor is still being procured from the manufacturer country. It is open secret that some areas of Bangladesh are rich in uranium but there are no authentic data. Moreover, very poor drives are observed to quantify uranium in different matrices. However, it is known that the neighboring country India has a big uranium deposit at its West Khasi Hills in Meghalaya District which is adjacent to the north part of Bangladesh. Almost alike geological structure is raising hope of having uranium deposits at least in that part of Bangladesh. To clear the facts and concurrently to reach the goal, a plan has been taken to search uranium in different locations of Bangladesh and in parallel to quantify uranium concentrations in the chosenmatrices such as water, soil, beach sand, rock and stones. By this time, the existing trace analytical laboratory of Bangladesh Atomic Energy Commission (BAEC) has gained the capability in determining uranium concentrations in trace level in different matrices by utilizing its previous experiences on the electrochemical techniques [5, 6].

Trace level uranium determination by electrochemical means is an innovative technology. High sensitivity of voltammetric techniques such as various forms of stripping voltammetry are found enable to quantify uranium with relatively simple and less expensive way [7]. Among stripping voltammetry, the adsorptive stripping voltammetry is reported to be a powerful technique applicable for trace uranium analysis [8]. In this technique,

at first uranium is preconcentrated on to the surface of a fresh mercury drop at a fixed potential by adsoorption and then followed it for measurements in between a chosen potential regions. To minimize the bad impact of other electroactive species, when they are remarkably present in the interested sample, and concurrently to enhance the efficiency of the technique, nowadays various complex forming organic ligands are utilized too. Among them catechol [9], oxine [10], cupferron [7,10,11], 2, 6-pyridinedicaboxylic acid [12], aluminon [13], pyromellitic acid [14], thioglycolic acid [15], chloranilic acid [11,16-20] etc. are extensively investigated. In case of chloranilic acid (CAA), at an optimum experimental condition, its adsorption range of potential onto a mercury drop and the mechanism of formation of U(VI)-CAA complex are found out [11,17]. The limiting concentration of uranium to be determined by using CAA is also proposed [11]. These valuable findings and information enable one to apply its relatively selective accumulation at potentials where usual nonionic organic contaminants and all other metal-CAA complexes are hardly adsorbed [11,16]. Moreover, besides for ground water and sea water this technology was successfully applied for the determination of uranium in soil [10], uranium alloy and analytical grade salts [14], slag heap drainage [17], lichens [19], sewage of uranium slag heap [19], waste water [15],etc.

The present study attempts to determine uranium in the water of a stream branch, beach sand and rocks by applying trace uranium determination technologystripping voltammetry. It seems that this study will be the first work on the determination of uranium in beach sand and rock samples using U(VI)-CAA complexation technique through differential pulse cathodic stripping voltammetry (DPCSV).

2. EXPERIMENTAL

2.1. Apparatus

Uranium concentration determination was carried out by utilizing Princeton Applied Research (PAR) model 174A polarographic analyzer, PAR 303 hanging mercury drop electrode (HMDE) as the working electrode, Ag/AgCl (saturated KCl) as the reference electrode and a platinum wire as the counter electrode. An XY recorder of model RE0089 was used for recording the voltammograms of the reduction of U(VI)-CAA complex. A magnetic stirrer of Model 305 was used for the homogeneous mixing of the samples and added uranium with the electrolyte solutions

in the cell sample cup. A Metrohom-692 digital pH meter was used for the pH measurements.

2.2. Chemicals

All the chemicals used in the present investigations were of analytical reagent grade or ultrapure and utilized without further purifications. Doubly distilled water passing through a quadruple deionizer column for extra pure water system with distillation plant was used to prepare the reagent solutions, and for rinsing the necessary glass wares and the three-electrode cell. 1000 ppm uranium standard solution (acidified with HNO_3) of volume 100 ml was prepared by dissolving appropriate amount of Uranyl Nitrate $[UO_2(NO_3)_2.6H_2O]$ (May and Baker Ltd., Dagenham, England). 100 ml 0.01M Chloranilic acid (CAA) (Alpha Aesar, USA) solution, 100 ml 0.01M EDTA solution, 250 ml 0.2M KNO_3 solution, 100 ml 1M HNO_3, 50 ml 5M HNO_3, 100 ml 1M NaOH and 100 ml 2M HF were also prepared.

2.3. Sample preparation

The stream water samples were collected in clean and acid washed polythene bottles from the stream branch which is flowing through the hills of the north-east area of Bangladesh and it is located near the border of India. Collected samples were immediately acidified by adding separately 100 μl of 1M HNO_3. After carrying the samples in the laboratory, these were kept in a refrigerator. Before voltammetric study, the samples were filtered through cellulose acetate filter paper of porosity 0.45 μm in view to separating any plotting and particulate materials.

Beach sand samples were collected in clean polythene bags from the Cox's Bazar, Chittagong and Kuakata beaches of the Bay of Bengal. The Bay of Bengal is located to the south part of Bangladesh. Samples for voltammetric studies were prepared by microwave digestion of the sands. At first, sands were oven dried to a constant weight at 333 K. For a sample about 0.5 g of sands was taken into a container made of perfluoroalkoxy polymer and treated by 2 ml 2M HF and 3 ml 5M HNO_3 for 12 h. The container with the generated mass was then placed in the microwave pressure vessel. There 10 ml 5M HNO_3:2M $HClO_4$ (4:1v/v)was added with the mass and then digested it at 180°C for 10 minutes. After cooling, the generated solution was filtered through a 0.45 μM syringe and diluted to 100 ml by adding water. Before adjusting this volume, the pH

value of the diluted solution was adjusted to 2.5 by adding 1M NaOH drop wise and constant stirring.

Rock sampleswere collected in clean polythene bags from different locations of the hilly areas of Bangladesh.Samples were immediately kept in a lead sheet container. After carrying, these were stored with care in the Health Physics and Radioactive Waste Management Unit (HPRWMU) of BAEC. It is worthy to mention here that during the field survey, therock samples showed remarkable but varying ranges of count rates compared to the background count rate. Such a behavior was taken as the indication that the rock samples consist of radioactive element(s). To ascertain the fact, it was essential to find out the radioactive element(s) and their activity if any instrumentally. To do so, the rocks were separately crushed and then grinded to powder in a PTFE mortar with high caution. Then the powders were separately subjected toγ-ray spectroscopy study but for a short period. The obtained γ-spectrums confirmed the presence of uranium in the rocks and gave information about the approximate uranium contents in them. This information was used during the preparation of samples for the voltammetric studies. Samples for the voltammetric studies were prepared by microwave digestion of the rock powders. The sample preparation procedure was almost identical to that applied for making beach sand samples as described in the preceding paragraph. In these cases, weights of rock powders taken for digestion were varied from 0.2 to 0.5 g. The sample volume and sample pH value were kept to constant to 100 ml and 2.5, respectively.

2.4. Procedure

25 ml 0.02 M KNO_3electrolyte solution was prepared from 0.2 M KNO_3 solution by dilution. Then 0.5 ml CAA and 50 μl EDTA solutions were added with it. The pH value of this mixture solution 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 CAA and EDTA downed to 1.95×10^{-4} M and 1.95×10^{-5} M, respectively. Then 10 ml mixture solution was pipetted into the cell cup and set it to the three-electrode cell system of the voltammetric analyzer. The mixture solution was then deaerated with nitrogen for 10 minutes under stirring condition. The stirrer was then switched off and for stripping analysis deposition potential was set to + 90 mV. After then on a large sized and fresh mercury drop, the accumulation of CAA,and concurrently U(VI)-CAA complex if any trace uranium is present in the

mixture solution, 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 the 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 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. There after- successively set up the deposition potential, produce a fresh mercury drop, completion of accumulation, set up scanning potential rage, start scanning and a voltammogram for the U(VI)-CAA complex reduction peak-for the first standard addition was obtained. In such a way five consecutive uranium standard additions were carried out with a view to getting U(VI)-CAA complex reduction peak current vs. uranium concentration behavior. Then the cell cup was taken out and the cell was cleaned repeatedly with 0.01M HNO_3 and water. By this time, a new cell cup made ready with the formerly prepared 10 ml mixture solution. The total experiment was then repeated with a view to testing the reproducibility of the studyat theset experimental conditions.

In case of stream water, 10 ml water sample was diluted to two times by using equal volume of 0.04 M KNO_3 solution. So, the concentration of KNO_3 electrolyte became to 0.02 M. Its pH value was adjusted to 2.5 by adding HNO_3 drop wise and stirring during the dilution. Then 10 ml solution was pipetted into the cell cup and set it to the three-electrode cell system of the voltammetric analyzer. After then 0.2 ml CAA and 20 µl EDTA solutions were added with it. As a result, the concentrations of CAA and EDTA in the cell cup downed to about 1.96×10^{-4} M and 1.96×10^{-5} M, respectively. After that all the successive steps starting from deaeriation to sketching voltammogramas carried out earlier were followedand the U(VI)-CAA reduction peak for the unknown uranium present in the stream water solution was obtained. There after uranium standard addition was continued for three times (10 ppb, 15 ppb and 20 ppb). From the peak current vs. uranium concentration relationships of the U(VI)-CAA reduction peaks, the amount of uranium present in the stream water solution in ppb level was obtained. Using this value, uranium contained in 10.22 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 5 ml stream water sample. From it uranium present per liter stream water was calculated.

In case of beach sand 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 CAA, 20 µl EDTA and 200 µl sand sample solutions were added with it. After that by adopting earlier procedure voltammograms of U(VI)-CAA reduction peak for the unknown uranium and three successive uranium standard additions (10 ppb, 20 ppb and 30 ppb) were obtained. The peak current vs. uranium concentration relationships of the U(VI)-CAA 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 200µl beach sand sample. From this value uranium present in 100 ml prepared sample was calculated. This amount of uranium is present in the digested amount of beach sand. Using this value, the amount of uranium present per Kg beach sand was obtained.

In case of rock samples, 100 µl rock digested sample was added with 10 ml mixture solution having same molarity of KNO_3, CAA and EDTA. Voltammograms for the unknown sample and three successive uranium standard additions (10 ppb, 20 ppb and 30 ppb) were drawn. From the peak current vs. uranium concentration relationships of the U(VI)-CAA 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 rock digested solution. By using this value, the amount of uranium present in the digested amount of rock and then uranium present per Kg rock was obtained.

3. RESULTS AND DISCUSSIONS

It was pointed earlier that the attempt of the present study was to determine the concentrations of uranium in the sand and rocks by adopting trace level uranium determination technique 'adsorptive stripping voltammetry'. With a view to gaining success, at first a method was optimized by following the best optimization value reported by others for the trace uranium determination using U(VI)-CAA complexation technique

[10-12,16-19] which was briefly described earlier in the introduction and experimental sections.

Figure 1 shows the adsorptive cathodicstripping (ACS) voltammogramsobtained forthe U(VI)-CAA complex reduction at different uranium concentrations, at the set experimental conditions. It can be seen that a well defined U(VI)-CAA complex reduction peak is appeared in between the potential range of – 55 mV to – 125 mV. Reduction peak current value gradually increased with increasing the concentrationsof uranium. It may be seen that with increasing uranium concentrations, the peak potential gradually shifted towards the positive potential direction. For 10 ppb uranium standard addition, the peak potential value is – 90 mV whereas for 60 ppb standard addition the value shifted to – 84 mV. Such a shifting of peak potentials with increasing uranium concentration seems to be a common matter. Shifting of peak potential from – 120 mV to – 100 mV was reported earlier [16].However, the appearance of U(VI)-CAA reduction peak at least 10 mV positive potential than that reported earlier seems due to introducing of 0.02M KNO_3 electrolyte newly in the measurement medium. It is reported that at low pH value, KNO_3 electrolyte shows huge tendency to shift the peak potential to the anodic direction [21]. The inset Figure(a) shows the peak current vs. uranium concentration relationships of the U(VI)-CAA complex reduction. It can be seen that the relationships show linearity up to 42-43 ppb added uranium with R^2 value of 0.996 beyond which a clear non-linearity is appeared. This is really a long linearity range and seems will allow the method to be used to measure unknown sample having attractive amount of uranium in trace level.
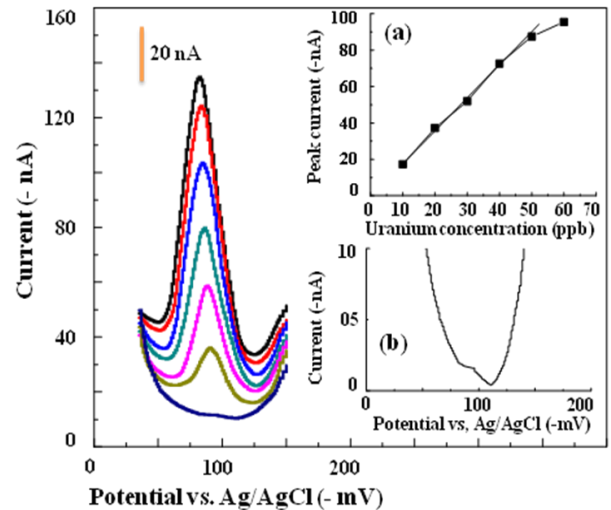
Figure 1: ACS voltammograms of the U(VI)-CAA reduction during uranium standard additions (0, 10, 20, 30, 40, 50 and 60 ppb) at pH 2.5 in presence of0.02M KNO$_3$, 1.95 x 10^{-4}MChloranilic Acid (CAA) and 1.95 x 10^{-5}M EDTA. Inset Figures: (a) Relationships between the U(VI)-CAA reduction peak current and concentration of uranium standard and (b) Voltammogram appeared for the blank solution.

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 [18]. The method was used to quantify uranium in the lichen sample. It is known that lichen is rich in different metal ions. But no remarkable interferences of the unwanted metals there in was observed. Nevertheless, present study informs that 42-43 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. Therefore, in the present study for the case of high uranium consisting sample, the sample must be diluted as the linear concentration range not exceeded during the standard additions.The inset Figure(b) shows the enlarge version of the fraction of voltammogram obtained for the mixture i.e. blank solution. The appearance of a very small peak hump in the voltammogram 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, themixture of the set electrolyte, reagents and ligands to be applied to quantify uranium concentrations in the targeted samples in trace level.

Figure 2 shows the adsorptive stripping voltammograms of the U(VI)-CAA complex for stream water sample with 10 ppb, 15 ppb and 20 ppb uranium standard additions. It may be seen that a smooth and a well definedvoltammogram 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)-CAA complex when 10 ppb uranium standard was added in the mixture solution as shown in Figure 1. It informs that the stream water sample consists of uranium. It may be seen that with increasing uranium standard, the reduction peak current gradually increased and the peak position slightly shifted to the positive potential direction. This behavior is analogous to that observed for the voltammograms when unknown sample was not added in the experimental cell cup, as shown in the Figure 1.
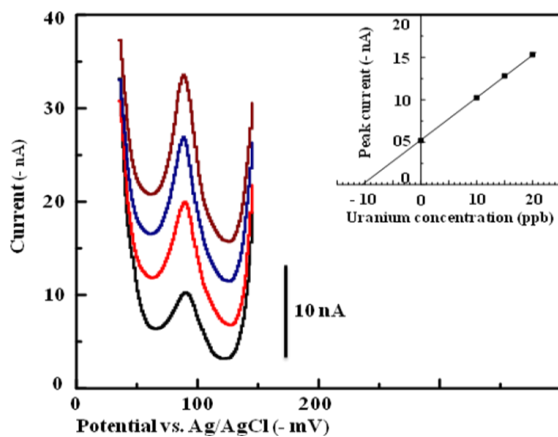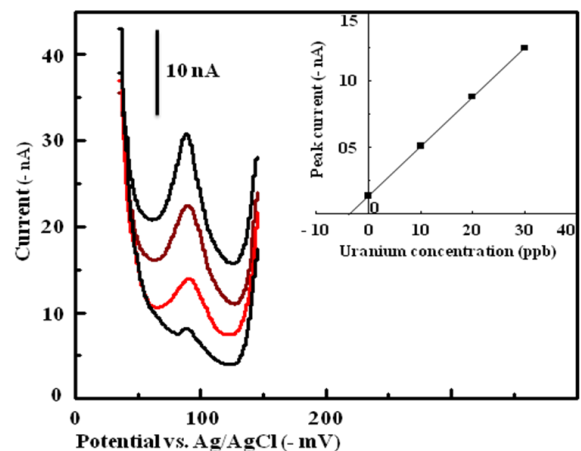

Figure 2: ACS voltammograms of the U(VI)-CAA reduction for stream water sample with 10, 15 and 20 ppb uranium standard additions at pH 2.5 in presence of 0.02M KNO$_3$, 1.95 x 10^{-4}M CAA and 1.95 x 10^{-5}M EDTA. Inset Figure: Relationships between the U(VI)-CAA reduction peak current and concentration of uranium.

The inset Figure shows the peak current vs. concentration relationships of the U(VI)-CAA complex reduction. It may be seen that peak current vs. concentration shows a linear relationship. The linear line passes through the peak current line (Y-axis) and touches the uranium concentration line (X-axis) at the concentration of 10.3 ppb. It means that 5 ml stream water sample consists of105.27 ng uranium (solution volume in the cell cup was 10.22 ml). Therefore,21.05μg uranium is present in one liter of stream water i.e. uranium concentration in the

stream water sample is 21.05 ppb. This value is quite high compared to the recommended value of WHO [4] but lower than that of EPA [3]. It is notable that the peoples of the hilly area are directly drinking this water and using it for their cooking and daily works. It seems that it is an alarming issue for the country.
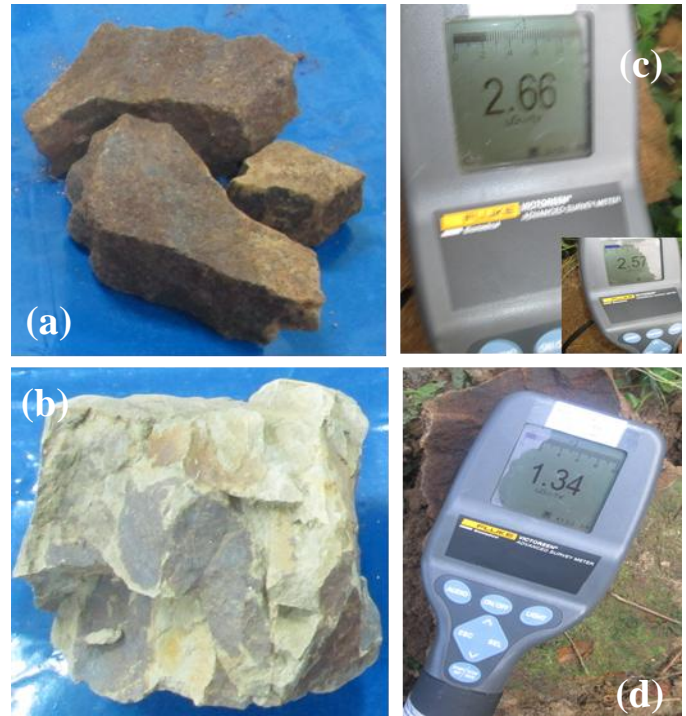
Figure 3 shows the adsorptive stripping voltammograms of the U(VI)-CAA complex for 200 μl beach sand digested sample (Kuakata) with 10 ppb, 20 ppb and 30 ppb uranium standard additions. The amount of sand sample taken for the microwave digestion is listed in the Table 1. The amounts were fixed up by carrying out a series of ACS analysis on the reduction behavior of the U(VI)-CAA complex. It can be seen that a smooth and a well definedvoltammogram with a reduction peak is appeared for the sample. The appearance of such a smooth peak is obviously the positive effect of appropriate dilution (1:52 fold) of the sample and the use of EDTA which will be explained later. However, the appearance of the U(VI)-CAA reduction peakinforms that the added beach sand digested sample consists of uranium. With increasing uranium concentration, increase in peak current behavior is analogous to that observed for the stream water sample (Figure 2) and for without unknown sample (Figure 1).

Figure 3: ACS voltammograms of the U(VI)-CAA reduction for beach sand sample (Kuakata) with 10, 20 and 20 ppb uranium standard additions at pH 2.5 in presence of 0.02M KNO$_3$, 1.95 x 10^{-4} M CAA and 1.95 x 10^{-5}M EDTA. Inset Figure: Relationships between the U(VI)-CAA reduction peak current and concentration of uranium.

The inset Figure shows the reduction peak current vs. concentration relationships of the U(VI)-CAA complex. The linear line of the peak currents vs. concentration touches the uranium concentration line (X-axis) at the concentration of 3.8 ppb. It means that 200 μl sand 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 19.8 μg. This amount of uranium is present in 0.5006 g of sand which corresponds to 39.55 mg uranium/Kg sand i.e. 39.55 ppm uranium in the sand of the Kuakata beach. Table 1 summarizes the uranium content found in the sands of other two beaches Cox's Bazar and Chittagong. The observed values are quite high and may be harmful for the tourists visited in the beaches. It seems that it is another alarming issue for Bangladesh.

Figure 4(a,b) shows two categories of rocks which were collected from the north-east area of Bangladesh adjacent to the neighboring country India. It is worthy to mention here that the rocks were categorized depending on their existing body count rates and the tentative uranium concentrations information obtained from the γ-ray spectroscopy studies. Rock 'a' stands in the high category and rock 'b' in the low category groups. Figure 4(c,d) represents some survey meter readings shown by the materials of the rocks in the spot. The values 2.66μSv/h, 2.57 μSv/h and 1.34μSv/h are almost 7-14 times higher than that of the back ground level. It is notable that in case of rock(a), the survey meter reading crossed the value 4.0μSv/h.

Figure 4. Photographs of two categories of rocks (a and b) collected from different locations of Bangladesh; (c and d) Survey meter readings of some rocks in the spot of survey.

Figure 5 shows the adsorptive stripping voltammograms of the U(VI)-CAA complex for 100 μl rock digested sample with three successive uranium standard addition (10, 20 and 30 ppb). The amounts of rock powders were taken for the microwave digestion 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)-CAA complex. The main purpose of the 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)-CAA complex. To achieve success, the experimental pH value, CAA ligand concentration, U(VI)-CAA complex accumulation potential, deposition time etc. were tested by adopting from the available reports and were applied as the system optimized value. It was observed that the optimized conditions were enabled in suppressing side effect of foreign materials on the U(VI)-CAA complex. One important factor was that present study additionally used 1.95×10^{-5}M EDTA solution. It was done in view to

inactivate the unwanted metal ions especially Cu(II), Fe(III), Mn(II), Zn(II) and Pb(II) ions present in the digested sample [9,10].

From the Figure 5, it can be seen that a well definedvoltammogram with a reduction peak is appeared for the unknown rock 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 [9,10]. 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)-CAA complex when 10 ppb uranium standard was added as shown in Figure 1. It may be taken as an indication that the sample consists of uranium. However, in the present case the fact is known. Y-ray spectroscopy study had cleared it.
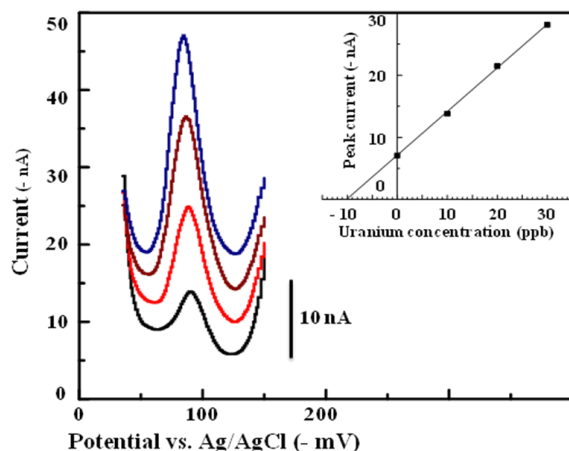

Figure 5: ACS voltammograms of the U(VI)-CAA reduction for rock digested sample (rock a) with three successive uranium standard additions (10, 20 and 30 ppb) at pH 2.5 in presence of 0.02M KNO$_3$, 1.95 x 10^{-4}M Chloranilic Acid (CAA) and 1.95 x 10^{-5}M EDTA. Inset Figure: Relationships between the U(VI)-CAA reduction peak current and concentration of uranium.

From the Figure, it can be seen that with increasing uranium standard, the reduction peak current gradually increased and the peak position slightly shifted to the positive potential direction as observed earlier experiments. The inset Figure shows the reduction peak current vs. concentration relationships of the U(VI)-CAA complex. Linear line of the peak currents vs. concentration touches the uranium concentration axis (X-axis) at the concentration of 9.8 ppb. It means that 100 μl rock(a) digested sample consists of101.14 ng uranium (volume in

the cell cup is 10.32 ml). So, amount of uranium in 100 ml prepared sample is 101.14 μg. This amount of uranium is present in 0.1908 g of rock(a) which corresponds to 530.08 mg uranium/Kg rock i.e. 530.08 ppm.

Figure 6 shows the adsorptive stripping voltammograms of the uranium(VI)-CAA complex reduction for 100 μl rock digested sample with three successive uranium standard additions (10, 20 and 30 ppb) for the rock(b) as shown in Figure 4. The voltammograms are analogous to that observed for the rock sample(a) (Figure 5). Inset Figure shows the peak current vs. concentration relationships. This relationship indicates the concentration of uranium in the system is 5.3 ppb. It informs that 100 μl added sample contains 54.69ng uranium. So 100 ml prepared solution consists of 54.7 μg uranium. This amount of uranium is present in 0.5023 g of rock which corresponds to 108.89 ppm uranium in the rock (b) of Figure 4.
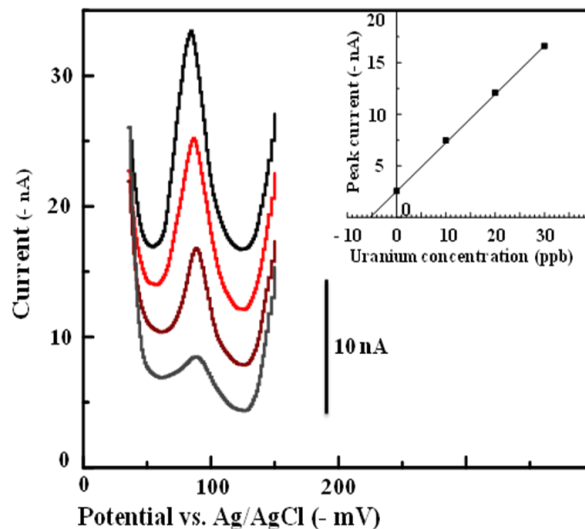

Figure 6: ACS voltammograms of the U(VI)-CAA reduction for rock digested sample (rock b) with three successive uranium standard additions (10, 20 and 30 ppb) at pH 2.5 in presence of 0.02M KNO$_3$, 1.95 x 10^{-4} M Chloranilic Acid (CAA) and 1.95 x 10^{-5}M EDTA. Inset Figure: Relationships between the U(VI)-CAA reduction peak current and concentration of uranium.

Table 1

Data for the amount of digested beach sand and rocks, volume of sample prepared, volume of sample added, uranium concentration obtained in ppb level and the amount of uranium in beach sand and rocks in ppm and the concentration of uranium in stream water.

Sample identification	Weight of digested rocks (g)	Sample volume made (ml)	Added sample volume (μl)	Uranium concentration (ppb)	Uranium concentration/kg stone (ppm)
Stream water	-	10.22	5×10^3	10.3	-
Beach sand:					
Cox's Bazar	0.5006	100	200	3.6	37.45
Chittagong	0.5013	100	200	3.6	37.42
Kuakata	0.5009	100	200	3.8	39.55
Rock:					
a	0.1908	100	100	9.8	530.08
b	0.5023	100	100	5.3	108.89

4. CONCLUSIONS

The present study demonstrates that cathodic adsorptive stripping voltammetric determination of uranium based on accumulation of the U(I)-CAA complex can be used to quantify uranium concentration in stream branch water, sea beach sand and uranium rich rocks by measuring uranium in trace level at first. It seems that the adopted experimental optimum conditions are quite suitable to minimize the interferences of other metal ions present in the stream water and especially beach sand and rocks 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 searching and quantification work of Bangladesh. However, this study seems the first work in this area, therefore it needs more investigations because beach sands and rocks of different area and different country may contain different elemental compositions and may impart different complexities in the measurements.

ACKNOWLEDGEMENTS

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