

Determination of uranium in stones by stripping voltammetry following adsorptive accumulation of the U(VI)-chloranilic acid complex

A. K. M. Atique Ullah¹, Md. Ibrahim Khalil², A. K. M. Fazle Kibria^{3*}

¹Scientific Officer, Chemistry Division, Atomic Energy Centre, Ramna, Dhaka 1000, Bangladesh Atomic Energy Commission

²Principal Geologist, Nuclear Minerals Unit, Atomic Energy Research Establishment, Savar, Dhaka 1349, Bangladesh Atomic Energy Commission

³Chief Scientific Officer, Nuclear Safety, Security and Safeguards Division, Sher-e-Bangla Nagar, Agargaon, Dhaka 1207, Bangladesh Atomic Energy Commission

*Corresponding author; E-mail: kibriaf@yahoo.com

Abstract - An attempt has been taken to determine the uranium contents in uranium rich stones, collected from different locations of Bangladesh, by adopting trace uranium determination technique. The technique is based on adsorptive accumulation of the uranium(VI)-chloranilic acid (CAA) complex onto a hanging mercury drop electrode, followed by reduction of the complex by cathodic voltammetric scan using differential pulse modulation. The used optimum conditions were pH value 2.5, CAA concentration 1.95×10^{-4} M, deposition potential + 90 mV, deposition time 120 s, scanned potential range - 35 mV to - 150 mV, pulse amplitude 25 mV and scan rate of 2 mV/s. 0.02M KNO₃ solution was used as electrolyte and EDTA solution of concentration 1.94×10^{-5} M was used with view to reducing the interferences of unwanted metal ions present in the stone digested samples. The U(VI)-CAA complex reduction peak current (i_p) vs. added uranium concentration (C) showed a linearity up to 43 ppb with a limit of detection of 0.316 ppb. 100 μ l volume of stone digested sample, in the investigation cell down to 100 fold dilutions, allowed to determining unknown uranium concentrations in the trace element level. The unknown concentrations appeared in ppb level and were 6.3 and 8.4 ng/ml, respectively. On calculation, uranium concentrations of the stones were found to be 211.47 and 127.98 ppm. The present attempt seems to be the first investigation on the quantification of uranium in stones using differential pulse cathodic stripping voltammetry (DPCSV). The optimum conditions aforementioned were used to determine uranium concentration in sea water. The value found to be 3.3 ppb and comparable to the reported values.

Key Words: Uranium, stone, U(VI)-CAA complex, adsorptive accumulation, DPCSV, EDTA, sea water.

1. INTRODUCTION

Uranium is one of the naturally occurring radioactive elements. Usually it exists in rock, stone, soil, sand and water. In nature, generally it is found in the form of isotopes with the quantity of U²³⁸ (99.27%), U²³⁵ (0.72%) and U²³⁴ (0.01%). Uranium consists of some special nuclear properties which were found usable for the benefit of human beings. But egoistic and caution less application of it be the cause of massive destruction and in parallel may emerge as a toxic epidemic entity for mankind through its dispersion and contamination [1,2]. Keeping all these in mind, now a day, uranium is considered to be a God gifted element for the mankind because of its highest energy production nature and in parallel high industrial demand worldwide. However, it is recorded that uranium has been using industrially as a nuclear fuel for more than five decades and seems to be used up to far future. At the end of 2012, a total of 437 commercial nuclear reactors required some 61980 tons of uranium. World annual reactor related uranium requirements are projected to be rise to between 72000-122000 tons by 2035 [3].

Environment i.e. soil, vegetations, aquatic media, air and thereby human body can be contaminated by the uranium released from different sources in various ways. The main sources can be taken as the effluent of nuclear industries, leached uranium from uranium rich rock, soil and sand, and dispersed uranium from its mine due to mining and transportations. Permissible intake level of uranium is very low and it is too low for drinking stuffs. In drinking water, EPA suggests maximum contaminant level 30 ppb [4] and WHO strictly recommended the level 15 ppb only [5]. Therefore environmental monitoring of uranium up to trace level is very important. On the other hand extraction

of more uranium, obviously with high caution, for industrial application is essential too. Therefore, worldwide scientists have been extensively doing research on environmental monitoring and in parallel searching the existence of uranium in its probable mediums for extraction [3].

Bangladesh badly needs the exploration of uranium as a fuel for its future nuclear power industry. It has a TRIGA MARK-II research reactor in running condition and its fuel material still is being procured from the outside. Although it is open secret that some areas of Bangladesh are rich in uranium but no authentic data is available. Moreover, very poor initiatives are observed to quantify uranium concentrations in different matrices. Actually, these were very essential work to meet up the future demand. To progress towards the goal, a plan has been taken to search uranium in different locations of Bangladesh and in parallel to quantify uranium concentrations appropriately in the collected samples such as water, soil, beach sand, rock and stones. With a view to succeeding the taken plan, Bangladesh Atomic Energy Commission (BAEC) has strengthened its electrochemistry laboratory through its Nuclear Safety, Security and Safeguards Division (NSSSD). By this time, the laboratory has gained capability in determining uranium concentrations in different matrices in trace level by utilizing its previous experiences on the electrochemical techniques [6]. Recently, an attempt has been taken to quantify uranium concentrations in uranium rich stones by adopting trace level uranium determination technology.

Trace level uranium determination by electrochemical means is almost a new 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 found 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 adsorption and then followed it for measurements in between a chosen potential regions. To minimize the hindering effect of other electroactive species, when they are remarkably present in the interested sample, and in parallel to enhance the efficiency of the technique, some complex forming organic ligands are utilized too. Among them catechol [9], oxine [10], cupferron [7,10,11], 2, 6-pyridinedicarbonylic acid [12], aluminon [13], pyromellitic acid [14], chloranilic acid [11,15-19] 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 [11,16]. 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 [11,15]. 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 [16], lichens [18], sewage of uranium slag heap [19], etc.

The present study attempts to determine uranium in uranium rich stones by adopting trace uranium determination technology. It seems that this study will be the first work on the determination of uranium in stone 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. 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 cup. A Metrohm-692 digital pH meter was used for the pH measurements.

2.2. Chemicals

All the chemicals used in this study were of analytical reagent grade or suprapur 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 reagent solutions and for rinsing glass wares and the three-electrode cell. 1000 ppm acidified uranium standard solution of volume 100 ml was prepared by dissolving appropriate amount of Uranyl Nitrate [$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] (May and Baker Ltd., Dagenham, England). 100 ml 0.01 M Chloranilic acid (CAA) (Alpha Aesar, USA) solution, 100 ml 0.01 M EDTA solution, 250 ml 0.2 M KNO_3 solution, 100 ml

1M HNO₃, 50 ml 5M HNO₃, 100 ml 1M NaOH and 100 ml 2M HF were also prepared.

2.3. Sample preparation

Stones collected from different locations of Bangladesh were stored in the restricted room of Health Physics and Radioactive Waste Management Unit (HPRWMU) of BAEC. During the field survey, these stones showed remarkable but varying count rates in the survey meter compared to the background count. It was taken as the indication that the stones consists of radioactive element(s). To ascertain the fact, the stones were separately subjected to 48 hours γ -ray spectroscopy study (short period study) in the HPRWMU laboratory. For this study, samples were prepared by crushing and then grinding the stones separately in a PTFE mortar with high caution. The obtained γ -spectrums confirmed the presence of uranium in the stones and gave information about their approximate concentrations. This information was used in case of the preparation of samples for the present study.

Samples for the determination of uranium using stripping voltammetry were prepared by microwave digestion. Crushed and grinded powders were oven dried to a constant weight at 333 K. Then depending on the approximate uranium concentration information, varying amounts of powders were digested. For a sample, at first powders were taken into a container made of perfluoroalkoxy polymer and treated by 2 ml 2M HF and 3 ml 5M HNO₃ for 12 h. Then it was placed in the microwave pressure vessel. There after 10 ml 5M HNO₃:2M HClO₄ (4:1v/v) was added and the sample was digested at 180°C for 10 minutes. After cooling, the solution was filtered through a 0.45 μ M syringe and diluted to 100 ml by adding water. Solution pH value was adjusted to 2.5 by adding 1M NaOH drop wise and constant stirring.

2.4. Procedure

In each case around 26.0 ml mixture solution of pH 2.5 containing KNO₃ electrolyte, CAA, EDTA and HNO₃ was made ready. At first 25 ml 0.02 M KNO₃ solution was prepared from 0.2 M KNO₃ solution. Then 0.5 ml CAA and 50 μ l EDTA solutions were added with it and pH value adjusted to 2.5 by adding HNO₃ drop wise and stirring. As a result, the concentrations of CAA and EDTA in the mixture became to about 1.95×10^{-4} M and 1.94×10^{-5} M, respectively.

10 ml mixture solution was pipetted into the cell cup and immediately set it up to the three-electrode cell system of

the voltammetric analyzer. There the mixture was deaerated with nitrogen for 10 minutes under stirring condition. Then the stirrer was switched off and for stripping analysis deposition potential was set to + 90 mV. After then on a large sized fresh mercury drop, the accumulation of U(VI)-CAA complex (if any uranium is present in the mixture) was continued for 120 s under stirring condition. Following the preconcentration, 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 from the XY recorder. Then 10 μ l uranium standard solution of concentration 10 ppm was added to the cell cup. It was made from 1000 ppm uranium standard solution by dilution. As a result, the standard addition became to 10 ppb uranium. The mixture was then stirred for 5 minutes and stopped. There after successively set up the deposition potential, fresh mercury drop made ready, completion of deposition, 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 done with a view to obtaining U(VI)-CAA complex reduction peak current (i_p) vs. uranium concentration (C) behavior. Then the cell cup was taken out and the cell was washed repeatedly with 0.01M HNO₃ and water. By this time, a new cell cup made ready with previously prepared 10 ml mixture solution. Then the total experiment was repeated with a view to testing reproducibility of the study.

In case of unknown sample, 10 ml mixture solution was deaerated and then 100 μ l sample (stone digested sample) was added to the mixture. The mass was then stirred for more 5 minutes with deaeration. After that all the successive steps as adopted earlier were completed and the voltammogram for the unknown U(VI)-CAA reduction peak was obtained. There after standard addition was continued for three times and sketched three voltammograms. From the i_p vs. C relationships of the U(VI)-CAA reduction peaks, the amount of uranium in ppb level was obtained. Using this value uranium contained in 10.1 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 μ l stone digested solution. By using this value, the amount of uranium presents in the digested amount of stone and then uranium present per Kg stone was obtained.

3. RESULTS AND DISCUSSIONS

Figure 1(a,b) shows two categories of stones which were collected from different locations of the north-east area of Bangladesh. The stones were categorized depending on their existing body count rates and the tentative uranium concentrations information obtained from the γ -ray spectroscopy studies. It was seen that the highest count rate showing stone showed the highest concentration of uranium in the γ -ray spectroscopy study and so on. Figure 1(c) shows a survey meter which is showing a count rate value of 2.41 μ Sv/h for the materials of a stone found during the survey at a hilly location. This count rate value is more than 12 times higher than that of the background level value. Such a count rate showing stone is presented in the Figure 1(a).



Figure 1. Photographs of two categories of stones (a and b) collected from different locations of Bangladesh; (c) A survey meter reading of a stone of category (a).

It was mentioned earlier that the attempt of the present study was to determine the concentrations of uranium in the stones as presented in the Figure 1 by adopting trace level uranium determination technique ‘adsorptive stripping voltammetry’. With a view to gaining success, at first a method was optimized by adopting the best optimization value reported by others for the trace uranium determination using U(VI)-CAA complexation technique [10-12,15-18] which is concisely described in the experimental section.

Figure 2 shows the adsorptive stripping voltammograms of the 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. Peak current gradually increased with increasing uranium concentrations. It may be seen that with increasing uranium concentrations, the peak potential slightly shifted towards the positive potential direction from - 90 mV to - 84 mV. Such a shifting of peak potentials with increasing uranium concentration seems to be a usual matter. Shifting of peak potential from - 120 mV to - 100 mV was reported earlier [15].

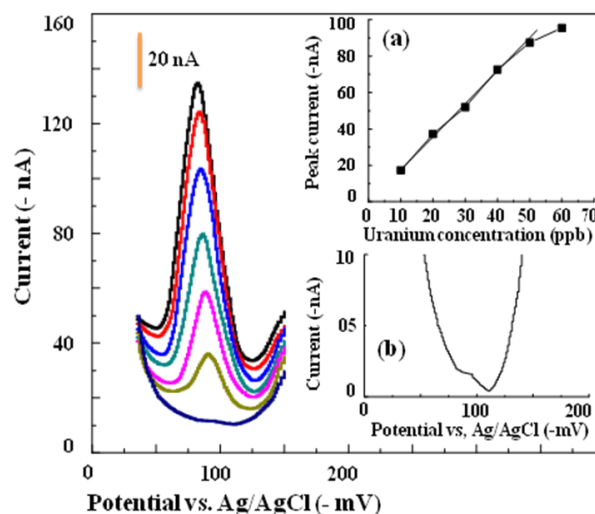


Figure 2: Adsorptive cathodic stripping voltammograms of the U(VI)-CAA reduction during uranium standard additions (0, 10, 20, 30, 40, 50 and 60 ppb) at pH 2.5 in presence of 0.02M KNO₃, 1.95 x 10⁻⁴ M Chloranilic Acid (CAA) and 1.94 x 10⁻⁵ EDTA. Inset Figures: (a) Relationships between the U(VI)-CAA reduction peak current and concentration of uranium standard and (b) Voltammogram appeared for the blank solution.

However, the appearance of U(VI)-CAA reduction peak at least 10 mV positive potential than that obtained earlier seems due to introducing of KNO₃ electrolyte newly in the measurement medium which was not used before. It is known that at low pH value, KNO₃ electrolyte shows a great tendency to shift the peak potential to the anodic direction [20]. The inset Figure(a) of the Figure 2 represents the i_p vs. C relationships of the U(VI)-CAA complex reduction. It may be seen that the relationships show linearity up to 43 ppb added uranium with R² value of 0.996 beyond which non-linearity is appeared. This long linearity range seems allow the method to be used to quantify unknown sample having handsome amount of uranium. Authors [17] have observed such a linearity up to 30 ppb uranium with R² value of 0.99 and up to 50 ppb

uranium with R^2 value of 0.89 and used the method to quantify uranium in lichen sample. It is notable that lichen is generally rich in different metals. Anyway, present study informs that 43 ppb is the limiting uranium concentration to be present in the investigated solution to avoid experimental error. Obviously this concentration 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 containing sample, the sample has to be diluted so that the linear concentration range will not be exceeded during the standard additions. The inset Figure(b) shown in the Figure 2 is representing the voltammogram appeared for the mixture i.e. blank solution. The appearance of a very small peak hump in the voltammogram is indicating that the used supporting solution and reagents are almost free from uranium contamination. It may be taken as the indication that without any major interruption effect, the mixture of set electrolyte and ligands to be applied to quantify uranium concentrations in the targeted stone samples (Figure 1).

The amounts of stone samples taken for the microwave digestion is listed in the Table 1. The amounts were fixed up by carrying out a series of stripping analysis on the reduction behavior of U(VI)-CAA complex.

Table 1

Data for the amount of digested stones, volume of sample prepared, volume of sample added, uranium concentration obtained in ppb (parts per billion) level and the amount of uranium in different stones in ppm (parts per million) and the concentration of uranium in sea water (water of the Bay of Bengal).

| Sample identification | Weight of digested stones (g) | Sample volume (ml) | Added sample volume (μ l) | Uranium concentration (ppb) | Uranium concentration/kg stone (ppm) |
|-----------------------|-------------------------------|--------------------|--------------------------------|-----------------------------|--------------------------------------|
| a | 0.3009 | 100 | 100 | 6.3 | 211.47 |
| b | 0.6629 | 100 | 100 | 8.4 | 127.98 |
| Sea water | - | 10 | - | 3.3 | - |

The main purpose of the series of analysis was to optimize the least volume of digested sample need to be added to the 10 ml mixture solution to obtain less than 10 ppb uranium concentration i.e. trace level uranium, and secondly to minimize as possible as the unwanted effect of other metal ions present in the sample on the desired U(VI)-CAA complex. To do it, 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. In parallel the optimization condition were capable in suppressing foreign materials side effect. One important factor is that present study additionally used an amount of EDTA (1.94×10^{-5} M). 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].

Figure 3 shows the adsorptive stripping voltammograms of the U(VI)-CAA complex for 100 μ l stone digested sample (added sample) with three successive uranium standard addition. The sample is for stone (a) as shown in Figure 1. 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 (1:100 fold) of the sample 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 (first addition) in the mixture as shown in Figure 2. It may be taken as an indication that the sample consists of uranium. However, in the present case the fact is known.

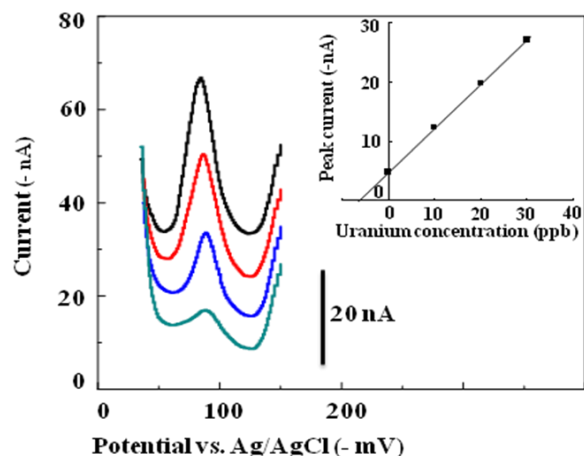


Figure 3: Adsorptive cathodic stripping voltammograms of the U(VI)-CAA reduction for stone digested sample (stone a) with three successive uranium standard additions (10, 20 and 30 ppb) at pH 2.5 in presence of 0.02M KNO_3 , 1.95×10^{-4} M Chloranilic Acid (CAA) and 1.94×10^{-5} EDTA. Inset Figure: Relationships between the U(VI)-CAA reduction peak current and concentration 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.

These behaviors are analogous to that observed for the voltammograms when sample was not added in the mixture i.e. in the cell cup, as shown in Figure 2. The inset Figure shows the i_p vs. C relationships of the U(VI)-CAA complex reduction. It may be seen that i_p vs. C shows a linear relationship. The straight line passes through the i_p line (X-axis) and touches the C-line (Y-axis) at concentration of 6.3 ppb. It means that the added 100 μ l stone digested sample contains 63.63 ng uranium (mixture volume in the cell cup is 10.1 ml). Therefore 100 ml stone digested sample consists of 63.63 μ g uranium which is present in 0.3009 g stone. Thus 1 Kg stone contains 241.47 mg uranium. So stone (a) of the Figure 1 consists of 241.47 ppm uranium.

Figure 4 shows the adsorptive stripping voltammograms of the uranium(VI)-CAA complex reduction for 100 μ l stone digested sample with three successive uranium standard addition for the stone (b) as shown in Figure 1. The voltammograms are analogous to that observed for the stone sample (a) (Figure 3). Inset Figure shows the i_p vs. C relationships. This relationship indicates the concentration of uranium in the system is 8.4 ppb. It informs that 100 μ l added sample contains 84.84 ng uranium which corresponds to 127.98 ppm uranium in the stone (b) of Figure 1.

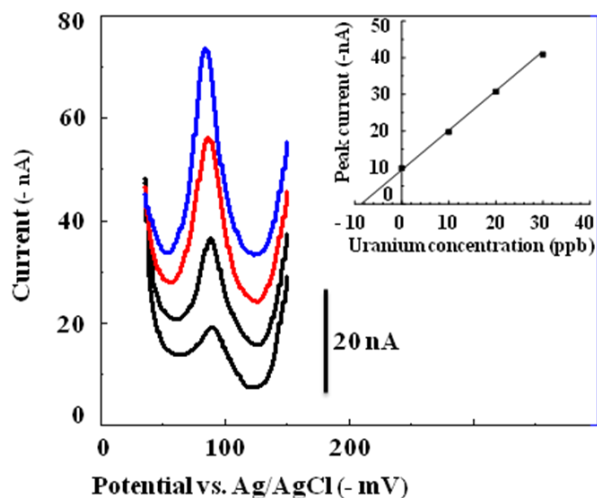


Figure 4: Adsorptive cathodic stripping voltammograms of the U(VI)-CAA reduction for stone digested sample (stone b) with three successive uranium standard additions (10, 20 and 30 ppb) at pH 2.5 in presence of 0.02M KNO_3 , 1.95×10^{-4} M Chloranilic Acid (CAA) and 1.94×10^{-5} EDTA. Inset Figure: Relationships between the U(VI)-CAA reduction peak current and concentration of uranium.

Figure 5 shows the adsorptive stripping voltammograms of the uranium(VI)-CAA complex reduction for the sea water of the Bay of Bengal. The Bay of Bengal is located to the south part of Bangladesh. In this study, the same experimental optimum conditions were adopted as those were used for the determination of uranium in the stone digested solutions. Calculated amount of high concentrated CAA, EDTA and KNO_3 solutions in 10 μ l volume range was added with sea water in view to preserving their similar concentrations as used for stone digested solutions. 10 ml sea water was directly used for the study. From the inset Figure it may be seen that 3.3 ppb uranium is present in the water of the Bay of Bengal. Authors [9] studied on the determination of uranium in Atlantic sea and Irish Sea water by using the ligand catechol and the values of 1.35×10^{-8} M and 1.32×10^{-8} M uranium were reported. These values are 6.78 and 6.63 ppb, respectively.

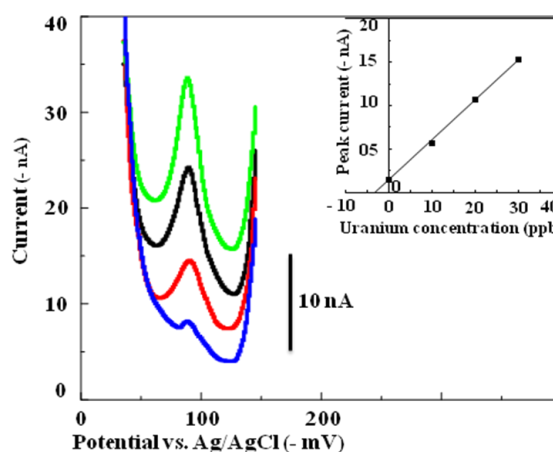


Figure 5: Adsorptive cathodic stripping voltammograms of the U(VI)-CAA reduction for the sea water of the Bay of Bengal with three successive uranium standard additions (10, 20 and 30 ppb) at pH 2.5 in presence of about 0.02M KNO_3 , 1.95×10^{-4} M Chloranilic Acid (CAA) and 1.94×10^{-5} EDTA. Inset Figure: Relationships between the U(VI)-CAA reduction peak current and concentration of uranium.

Gholivand and Nssab determined uranium in the sea water of the Persian Gulf using pyromellitic acid as ligand and found a value of 2.26 ppb [14]. Presently observed result is stands in between the reported values. This finding may be taken as the successful applicability of the used optimum conditions for the determination of uranium in sea water too.

4. CONCLUSIONS

The present study demonstrates that cathodic adsorptive stripping voltammetric determination of uranium based on accumulation of the U(II)-CAA complex can be used to quantify uranium concentration in uranium rich stones 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 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 searching and quantification work of Bangladesh. However, this study seems the first work in this area therefore it needs more investigations because stones of different area and different country may contain different elemental compositions and may impart different complexities. The same experimental condition may be used for the determination of uranium in sea water too.

ACKNOWLEDGEMENTS

The financial support from the Ministry of Science & Technology, Government of the People's Republic of Bangladesh, in the session 2014-2015 under special allocation (**No. Physical 261**), in the form of chemicals and small accessories, is thankfully acknowledged.

REFERENCES

- [1] INTERNATIONAL ATOMIC ENERGY AGENCY, *Status and Trend in Nuclear Education*, IAEA Nuclear Energy Series No. NG-T-6.1, IAEA, Vienna, 2011.
- [2] INTERNATIONAL ATOMIC ENERGY AGENCY, *The Management System for the Disposal of Radioactive Waste, Safety Guide*, IAEA Safety Standards Series No. GS-G-3.4, IAEA, Vienna, 2008.
- [3] *Uranium 2014: Resources, Production and Demand*, A Joint Report by the OECD Nuclear Energy Agency and the International Atomic Energy Agency, NEA No. 7209, OECD 2014.
- [4] U.S. EPA, *Draft Guidelines for Carcinogen Risk Assessment (Review Draft, July 1999)*, U. S. Environmental Protection Agency, Risk Assessment Forum, Washington, D.C., 1999.
- [5] World Health Organization (WHO), *Guidelines for Drinking Water Quality, Vol. 1, Recommendations*, 3rd Edition, WHO, Geneva, 2006.
- [6] M. E. Nabi, S. Z. Haider, M. A. Islam, A. H. Khan and A. K. M. F. Kibria, Stripping voltammetric studies of copper-glutathione complexation in sea water, *J. Ban. Academy Sci.*, vol. 23, pp. 207-217, 1999.
- [7] Joseph Wang and Rossi Setradji, Selective determination of trace uranium by stripping voltammetry following adsorptive accumulation of the uranium-cupferron complex, *Anal. Chim. Acta*, vol. 264, pp. 205-211, 1992.
- [8] M. I. C. Cantagallo and M. A. de Sousa, Voltammetric determination of uranium in rocks, soils and sediments by using the catalytic nitrate reduction, *J. Radioanal. Nucl. Chem.*, vol. 218, pp. 117-118, 1997.
- [9] Constant M. G. Van Den Berg and Zi Qiang Huang, Determination of uranium in sea water by cathodic stripping voltammetry of complexes with catechol, *Anal. Chim. Acta*, vol. 164, pp. 209-222, 1984.
- [10] Jianyan Wang, Joseph Wang, Jianmin Lu and Khri Olsen, Adsorptive stripping voltammetry of trace uranium: Critical comparison of various chelating agents, *Anal. Chim. Acta*, vol. 292, pp. 91-97, 1994.
- [11] L. Novotny, T. Navratil, S. Sander and P. Basova, Electrocapillary activity and accumulation of U(VI)-Cupferron and U(VI)-Chloranilic acid complexes on mercury electrode, *Electroanalysis*, vol. 15, pp. 1687-1692, 2005
- [12] M. B. Gholivand, H. Rashidi Nassab and H. Fazeli, Cathodic stripping voltammetric determination of uranium(VI) complexed with 2, 6-pyridinedicarbonylic acid, *Talanta*, vol. 65, pp. 62-66, 2005.
- [13] Ki-Won Cha, Chan-Il Park and Sang-Hyun Park, Simultaneous determination of trace uranium(VI) by adsorptive cathodic stripping voltammetry with aluminon ligand, *Talanta*, vol. 52, pp. 983-989, 2000.
- [14] M. B. Gholivand and H. Rashidi Nassab, Highly selective adsorptive cathodic stripping voltammetric determination of uranium in the presence of pyromellitic acid, *Electroanalysis*, vol. 17, pp. 719-723, 2005.
- [15] Sylvia Sander and Gunter Henze, Adsorptive voltammetric techniques for the determination of uranium(VI) with 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone as complex forming reagent, *Fresenius J. Anal. Chem.*, vol. 349, pp. 654-658, 1994.
- [16] Sylvia Sander, Wolfram Wagner and Gunter Henze, Direct determination of uranium traces by adsorptive stripping voltammetry, *Anal. Chim. Acta*, vol. 305, pp. 154-158, 1995.
- [17] Sylvia Sander, Wolfram Wagner and Gunter Henze, Possibilities for the automated determination of trace concentrations of uranium in water samples by adsorptive stripping voltammetry, *Anal. Chim. Acta*, vol. 349, pp. 93-99, 1997.

- [18] Sabyasachi Rout, Manish K. Mishra, Ajay Kumar and Pazhayath Mana Ravi, Determination of ultra trace uranium in lichen by adsorptive-cathodic stripping voltammetric technique, *Int. J. Environ. Sci.*, vol. 4, pp. 605-613, 2014.
- [19] Sylvia Sander, Simultaneous adsorptive stripping voltammetric determination of molybdenum(VI), uranium(VI), vanadium(V) and antimony, *Anal. Chim. Acta*, vol. 394, pp. 81-89, 1999.
- [20] H. P. Nirmaier, P. Schmoll, K. H. Bauer and A. Meyer, Ultratrace determination of uranium(VI) in drinking water by adsorptive stripping voltammetry according to DIN 38406-17: *Influence of pH and KNO₃ concentration*, Published by Metrohm, 2014.



A. K. M. Fazle Kibria has been doing R&D works in the Bangladesh Atomic Energy Commission (BAEC) since 1992. He is leading the research groups working on electrochemistry, nanomaterials and physical protection of nuclear materials. He obtained his Ph. D. degree from the Nagasaki University, Japan. He has more than twenty publications in different international reputed journals whose citations are around 400.