DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY STUDIES IN AQUEOUS SOLUTION OF Na₂CO₃ FOR THE DETERMINATION OF TRACE AMOUNTS OF CADMIUM PRESENT IN UO₂ FUEL

J.V. Kamat, N. Gopinath and S.K. Aggarwal
Fuel Chemistry Division
Bhabha Atomic Research Centre

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Cadmium possesses a high neutron absorption cross-section for thermal neutrons and therefore its presence in amounts greater than 1 ppm is not tolerated in UO₂ fuel. The technique to be used for its determination in the fuel as part of quality control should be selective and sensitive. The Differential Pulse Anodic Stripping Voltammetry (DPASV) technique coupled with Hanging Mercury Drop Electrode (HMDE) is ideally suited for determination of trace amount of cadmium in UO₂ fuel due to the fact that there is a large enhancement in the limit of elemental detection in stripping technique using mercury electrode.

The solid UO₂ sample is dissolved in HNO₃ acid for performing various quality control tests. This solution medium is unsuitable for the determination of cadmium in presence of UO₂²⁺ by Voltammetry technique because not only Cd²⁺ but also UO₂²⁺ will simultaneously take part in the electrode reaction since the value of redox potential of Cd²⁺, -0.434V, is less positive to that value of UO₂²⁺, +0.327V. As a result, the current efficiency of reduction of Cd²⁺ will be too small to be able to determine Cd in presence of very large excess of UO₂²⁺.

It has been observed recently in our laboratory that the value of the reduction potential of Cd²⁺ is more positive than that of UO₂²⁺ in saturated aqueous solution of Na₂CO₃.

This paper will discuss the results of experiments...
performed in Na₂CO₃ aqueous solution to develop a method and optimize the parameters associated with the Differential Pulse Anodic Stripping Voltammetry (DPASV) technique for the determination of trace amounts of cadmium present in UO₂ fuel.

The experimental procedure has been designed as follows. The size of the sample, UO₂, to be taken for determination of cadmium has been fixed at about one gram and should be dissolved quantitatively in minimum volume of dilute (1:1) HNO₃. Later, the solution has to be evaporated to near dryness and then the residue to be dissolved in 25 mL of Na₂CO₃ aqueous solution. Two aliquots, each of 10 mL (the minimum volume of solution required for all the three electrodes are in good contact with the solution) are to be taken for the purpose of determination of Cd.

It has been observed that the evaporated acid dissolved one gram UO₂ is completely soluble with the production of a clear solution in 25 mL of aqueous solution Na₂CO₃ of concentration 0.4 M and more. The concentration of UO₂²⁺ in this solution is about 0.15 M.

Stock solutions of 0.15 M UO₂²⁺, 0.35 mM Cd²⁺ (1 ppm) and a mixture of 0.15 M UO₂²⁺ and 0.35 mM Cd²⁺ (1 ppm) in 0.5 M Na₂CO₃ were prepared for use as test solutions in the appropriate experiments.

The values of peak reduction potential, Eₚᵣ, for Cd²⁺ and UO₂²⁺ in 0.5 M Na₂CO₃ aqueous solutions were determined by Linear Scan Voltammetry. It was found that the value for Cd²⁺, -0.776 V, was more positive by an amount of 0.25 V than that of UO₂²⁺, -1.025 V.

The optimum DPASV experimental parameters for the determination of Cd²⁺ in 10 mL volume of synthetic mixture solution containing both Cd²⁺ and UO₂²⁺ prepared in 0.5 M Na₂CO₃ aqueous solution were found to be dissolution of cadmium in HMDE at an accumulation voltage, E_acc, of –0.75 V (Ag/AgCl, 3 M KCl) for a duration of 600 s and followed by stripping it by changing the voltage of HMDE from –0.75 V to –0.60 V at a scan rate of 10 mV s⁻¹ superimposing a pulse voltage of 50 mV for 5 s.

The DPASV current peak heights were determined for different concentrations of Cd²⁺ (1 x 10⁻⁷ M to 3.9 x 10⁻⁷ M) in presence of 0.15 M UO₂²⁺ using the optimized experimental conditions. A linear relation between the values of DPASV current peak heights and their corresponding concentration of Cd²⁺ was observed. The value of correlation coefficient (R²) obtained was 0.94.

The developed methodology is suitable for the determination of trace amounts of cadmium in UO₂.

**ABOUT THE AUTHORS**

Ms. J.V. Kamat has obtained her M.Sc degree from Mumbai University. She joined Mass Spectrometry Section, Fuel Chemistry Division. After joining, she obtained her Ph.D from Mumbai University. She is involved in the application of electroanalytical techniques for developing methods for the analysis of elements of interest in nuclear fuels. She is the Treasurer of Indian Society for Electro Analytical Chemistry (ISEAC).
Mr. N. Gopinath has obtained M.Sc. Degree in Physical Chemistry from Sri Venkateswara University, Tirupati. He joined the Chemical Methods Group, Radiochemistry Division, BARC. Since then he is actively involved in developing and employing various Electroanalytical techniques for different applications in the nuclear fuel cycle. He is a co-author of a good number of scientific publications. He is the Secretary of the Indian Society for ElectroAnalytical Chemistry (ISEAC).

Dr. S.K. Aggarwal is presently Head, Fuel Chemistry Division, BARC. He received his B.Sc.(Hons) from Guru Nanak Dev University, Amritsar, in 1972 with two Gold Medals. He joined the 16th Batch of BARC Training School in 1972 and received Homi Bhabha Award. He did his Ph.D from Mumbai University in 1980. He is a co-author of about 300 scientific publications, which include 100 articles published in reputed journals. Dr. Aggarwal has participated in several international and national conferences and in different international intercomparison experiments. He is a specialist in the field of atomic mass spectrometry and alpha spectrometry and is interested in various mass spectrometry techniques. His other areas of interest include electrochemistry and solvent extraction. He represents India in the Executive Committee of International Mass Spectrometric Conferences. He has visited several countries in Europe, America and Australia as an expert as well as for delivering lectures. He is a recognized Ph.D. Guide of the Mumbai University.