Coulometric analysis of Uranium in solution through Boron Doped Diamond electrodes (BDD)

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Abstract

Controlled potential coulometry (CPC) is an analytical technique allowing for the accurate determination of an electroactive species in solution by measuring the amount of electricity used during its quantitative electrochemical oxidation or reduction. Connected only to physical standards, CPC is a primary analysis method which can attain uncertainties close to 0.1%. These uncertainties, as well as the small amount of analyte employed, have led to a resurgence in interest in CPC as a nuclear analysis technique in the field of metrology. In particular, the technique has been successfully employed for the determination of Pu amount content in reference materials. However, CPC is sensitive to the material of the working electrode used to perform the electrochemical reactions. Au electrodes –used for the analysis of Pu– display a narrow electrochemical window in acidic media, which excludes their use for the study of U by reduction. Historically performed using Hg – a material nowadays forbidden in the nuclear industry– the analysis of U by CPC remains a challenge in nuclear metrology. Amongst the modern electrode materials which could replace Hg, Boron Doped Diamond (BDD) possesses a good chemical stability and interesting electronic properties. In particular, its surface oxygen terminations inhibit the adsorption of molecules, leading to a low double layer capacitance as well as a large electrochemical window (-1.5 to +1.6 V/MSE in 0.5M H_2SO_4). These properties render BDD a promising alternative to Hg for the CPC analysis of U amount content in solutions. We present herein recent advances on the use of BDD for the determination of U amount content in sulphuric acid through CPC. Initially, the optimal experimental parameters for CPC analysis using BDD electrodes were determined through electrochemical studies. The applicability of BDD as an alternative to Hg was then studied through the CPC analysis of U standard solutions. As well as demonstrating its use in the CPC analysis of U, the results highlight the importance of BDD when compared to traditional working electrode materials. With its high versatility, BDD would allow to extend the technique to a large amount of analytes and, effectively, enhance its importance within the field of nuclear analysis.

1. Introduction

The first decades of the 21st century see humanity facing significant existential challenges from both the ever more important issue of climate change [1] as well as from the resurgence of cold-war era international power dynamics [2]. In particular, the geopolitical unrest arising from this latter factor has shone the spotlight once more on the risk of nuclear warfare and its tragic consequences. With an estimated global arsenal of over 9000 nuclear warheads [3] distributed across global players with differing, and often opposed, future objectives, the importance of nuclear safeguard operations as well as the UN brokered non-proliferation treaty cannot be overstated. In this context, the study of modern analytical methods for the analysis of actinides (most notably uranium (U) and plutonium (Pu) isotopes) has become one of the main missions of the French alternative energies and atomic energy commission (CEA)'s Committee for the Establishment of Analysis Methods (CETAMA). Throughout its existence, the CETAMA has worked with its metrological laboratory for nuclear matter, the LAMMAN, towards the development and validation of techniques for the analysis of actinides [4]. Amongst the methods historically employed for the analysis of Pu and U, controlled potential coulometry (CPC), has been the object of extensive research [5]–[7]. CPC has long been considered an interesting technique due to its underlying principles, which allow it to reach particularly low measurement uncertainties with small amounts of analyte [8], [9].

CPC is a method that allows to determine the quantity of an electroactive species in solution by measuring the amount of charge used by this species to undergo an electrochemical transformation. The technique relies on Faraday's law where the mass, *m*, of an element is related to the molar mass of the studied species,

M, the number of electrons exchanged during the electrochemical transformation of the species, n, Faraday's constant, F (equal to 96485.33212 C/mol [10]), and the quantity of electrical charge involved in the studied reaction, Q, as shown in equation (1).

$$m = \frac{QM}{nF} \quad (1)$$

Experimentally, Q is determined by integrating the amount of current used for the electrochemical conversion, over the time of analysis. Effectively relying solely on physical parameters (time and current), CPC is thus considered a primary measurement method. The technique's traceability to highly accurate physical standards means that excellent degrees of trueness and precision are obtainable [5].

The good performances of CPC have led to its adoption for the determination of Pu amount content in solutions through the study of the Pu^{IV}/Pu^{III} redox couple. At the CETAMA, the application of CPC for the routine determination of Pu content has been performed with uncertainties of 0.1 % (k=2) for pure Pu solutions [5] and 0.14 % (k=2) for mixed U:Pu solutions containing ratios of up to 100:1. [5]

Unfortunately, the technique's application to the analysis of U cannot be said to have reached similar successes. Indeed, although historically the coulometric determination of U amount content in solutions was shown to provide promising results [9], the complexities of working with this actinide have hampered its application. Due to the high stability of the uranyl cation (UO_2^{2+}) in aqueous acidic media, the $U^{VI/IV}$ redox couple is that which is generally studied during CPC. More specifically, it is the quantity of energy employed to reduce UO_2^{2+} to U^{4+} which is used for the determination of U amount content. However, in order to perform the reduction, a strongly negative potential needs to be applied to the studied systems. This potential lies below the hydrogen overpotential of traditional electrode materials (Au, Pt, and Ag) in acidic conditions, effectively rendering their use for the study of U by CPC impossible [11]. This limitation was commonly bypassed by the use of mercury (Hg) working electrodes whose more negative electrochemical window in acidic solutions allowed to perform the oxidation of the uranyl cation. Nowadays, the disposal of radioactive Hg waste in the nuclear industry has become impossible, effectively precluding the use of this material in CPC. As such, in recent years the technique's revival for the analysis of U solutions through alternative electrode materials has been a subject of study within the CETAMA.

Of the materials considered as alternatives to Hg for the coulometric analysis of U, Boron Doped Diamond (BDD) is that which was deemed the most promising. BDD is a synthetic carbon-based material whose electrical and physical properties can be controlled (and tailored) by varying its synthesis conditions (concentration of boron dopant, synthesis method …). [12]–[14] With its high chemical stability, large electrochemical window, and low double layer capacitance, BDD is particularly suited for the specific requirements of the coulometric determination of U amount content in acidic solutions.

The work presented herein aims to outline the research carried out by the CETAMA development of the coulometric analysis of U content of solutions through the application of BDD electrodes. Initially, cyclic voltammetry studies were performed, allowing not only to study BBD's electrochemical properties but also to establish preliminary experimental parameters for the material's application as a working electrode during the CPC analysis of U solutions. Finally, the applicability of the material to the analysis of U by CPC was demonstrated by studying certified reference material standard solutions with known U content.

2. Experimental Methods
2.1. Chemicals

The analytical grade chemicals used during the study – concentrated Nitric Acid (HNO_3, Merck, 68% ultrapur), concentrated sulfuric acid (H_2SO_4, Merck, 95-97% for analysis), sulfamic acid ($HOSO_2NH_2$, Merck, Emsure, $\geq$ 99.0%), sodium hydroxide (NaOH, Merck, 27%, for the determination of nitrogen)– were purchased from VWR.

$HOSO_2NH_2$ (1.5 mol L^{-1}), H_2SO_4 (0.5 mol L^{-1}), and HNO_3 (0.9 mol L^{-1}) solutions were prepared by diluting the concentrated reagents in deionised water ($\rho > 18$ MΩ cm).

2.1.1. U solutions

The pure U solutions studied corresponded to two samples of standard uranyl nitrate solutions (EQRAIN U n°12, vial K170; and EQRAIN U n°16, vial T054) supplied by the CETAMA's LAMMAN. The solutions are traceable to the CERAMA's OTU1 natural uranium oxide certified reference material. The EQRAIN U n°12 standard solution was determined to have a U content of (249.70 ± 0.25) g kg^{-1} (k=2), a density of (1.5712 ± 0.0002) g cm^{-3} at 20°C (k=2), and a free acidity of (1.48 ± 0.03) mol L^{-1} (k=2). The EQRAIN U n°16 standard solution was determined to have a U content of (196.61 ± 0.25) g kg^{-1} (k=2), a density of (1.4247 ± 0.0002) g cm^{-3} at 20°C (k=2), and a free acidity of (1.60 ± 0.03) mol L^{-1} (k=2). The isotopy of uranium corresponds to that of natural uranium and the uranium molar mass is equal, according to recent literature, to (238.02891±0.00003) g mol^{-1} [15].

For the coulometric analysis experiments, a diluted solution of U was prepared through two subsequent dilutions: firstly 1.3 ml of solution K170 were diluted in H_2SO_4 (0.1 mol L^{-1}, 18ml), after which 1 ml of this diluted solution was further diluted in H_2SO_4 (0.1 mol L^{-1}, 19ml). The final diluted U solution, henceforth referred to as K170-D2, was then subject to a drying procedure which allowed to eliminate potential impurities in the studied samples. This procedure is detailed in section 3.2.1 of this publication.

2.2. Electrochemical apparatus

The electrochemical analysis experiments presented were performed by using a three-electrode system composed of a working electrode (WE), a counter electrode (CE), and a reference electrode (RE) connected to a potentiostat and set in separated compartments.

For all experiments performed a PARSTAT 3000A (AMETEK instruments) potentiostat was used in combination with the supplied "Versastudio" software (version 2.60.6).

The pH of all of the studied solutions was measured by using a digital pH meter (Metrohm, 913 pH meter) calibrated by pH buffers of (7.00 ± 0.02) and (4.01 ± 0.02) values from Mettler.

2.2.1. Voltammetry studies

In order to characterise the response of BDD in the studied media, an electrochemical set-up with a rotating disc electrode (RDE) was used.

In this set-up a platinum (Pt) wire was used as CE whilst a saturated mercury sulfate electrode (MSE, Radiometer XR200 model, E (25°C) = 648mV/SHE) was used as the RE. The WE consisted in a RDE body (Radiometer EDI101) equipped with changeable tips. Three different electrode tips were used during this study: gold (Au, 2 mm diameter, sourced from Origalys), glassy carbon (GC, 3 mm diameter, sourced from Origalys), and BDD (8 mm diameter, ~10 µm thin film coated on a Nb substrate, sourced from CONDIAS GMBH).

2.2.2. Coulometric studies

Coulometric studies used a modified version of the three electrode coulometry system (EG&G model 377A coulometry cell system) previously presented in our work [7]. In the electrochemical set-up used during the present study a MSE (Radiometer – XR200 model) was used as the RE whilst a Pt mesh served as the CE. The WE for the coulometric studies consisted of two expanded Nb mesh sheets (single sheet dimensions: 50 mm by 30 mm, single sheet thickness: 1.3 mm) coated with a BDD thin film (5 µm thin film coated on a Nb substrate, sourced from CONDIAS GMBH) and connected in parallel.

Due to the volume of the electrochemical cell used, the whole surface area of the BDD WEs was not submerged in the studied solutions. As such, the electrochemically active surface area of the two BDD meshes had to be determined and was found to be (14.8 ± 0.6) cm^2 (i.e. circa 7.5 cm^2 per immersed BDD mesh). This was determined by applying the Randles-Sevcik equation to the electrochemical response of a 2.58 mmol L^{-1} potassium ferricyanide solution (purchased from VWR) with a volume equal to that of the analyte solutions used in the present experiment (33.5 mL) and by adopting a value of the diffusion coefficient of ferricyanide from literature [16].

The RE and CE were placed in individual electrolytic compartments filled with the same electrolyte used in the main compartment of the cell. The two BDD meshes composing the WE were placed in a parallel configuration 3 cm apart with the other cell components (CE, RE, and stirrer) located in between the two meshes. Vycor (EGG Kit, acquired from HTDS) glass frit membranes were used to establish an electrolytic junction with ultra-low leakage rates between the secondary cells and the main compartment of the analysis cell. The separation of the RE and CE from the analysed solutions limits the transport of products between the WE and the CE as well as minimising any contamination of the analysed solutions by the filling solution of the RE.

During experiments, the homogeneity of the solutions was ensured by using a paddle type stirrer (EG&G model 377 synchronous stirring motor) made of glass with a geometry optimised to avoid splashing.

In order to remove oxygen from the system, a constant flow of argon was maintained over the surface of the studied solutions. This flow of inert gas was humidified by a bubbler containing deionised water placed upstream from the electrochemical cell in order to prevent the bulk solutions from drying out.

3. Experimental procedures
3.1. Voltammetry studies

The voltammetry studies were performed using the electrochemical set up described in section 2.2.

3.1.1. Electrode pretreatment

Prior to performing any electrochemical studies, the BDD electrodes underwent a pretreatment procedure. As previously discussed in literature [14], this procedure is an essential requirement, allowing to condition the surface of the BDD and thus ensure a stable and reproducible response to the studied media. During the present experiment, the BDD RDE was immersed in a solution of H_2SO_4 (0.5 mol L^{-1}, 20 mL) and subjected to a series of 20 alternating galvanic pulses (2 mA cm^{-2} for 60s, followed by -2 mA cm^{-2} for 60 s). This pretreatment was performed daily prior to performing any experiments.

No pretreatment procedure was applied when utilising Au or GC WEs.

3.1.2. Cyclic voltammetry

A pretreated BDD WE was immersed a new H_2SO_4 solution (0.5 mol L^{-1}, 20 mL) to which a known volume (340 µL) of T054 was added. The pH of the created solution was measured and adjusted to the desired level through the dropwise addition of NaOH. The electrochemical response of the prepared solutions (U-containing, or background) was then analysed through cyclic voltammetry.

The response of the BDD WE was recorded at five different scan rates (250, 100, 50, 25, and 10 mV s^{-1}). Each scan was performed for two cycles, with the second cycle being retained for analysis.

The same cyclic voltammetry experiments were performed in H_2SO_4 (0.5 M, 20 mL) solutions without the addition of U to measure the blank response of BDD. The pH of the blank solutions was adjusted through the dropwise addition of NaOH to correspond to that of the U-containing samples. Identical experiments, studying the electrolyte's blank response, were also performed using the Au and GC working electrodes.

3.2. Coulometric analyses

For the coulometric analyses, the electrochemical set up described in section 2.2.2 was used in combination with the following procedure.

3.2.1. Sample preparation procedure

Four aliquots of U standard solution (solution K170-D2, circa 3 ml per sample) were weighed directly into the coulometric glass cells used for CPC analysis, such that each cell contained 3 mg of U. All mass measurements were corrected for air buoyancy in order to eliminate systematic errors.

Once the aliquots had been transferred and weighed, H_2SO_4 (1 mL, 3 mol L^{-1}) was added to each to stabilise the actinides as UO_2 (SO_4) during the fuming procedure. The created solutions were left to homogenise and react overnight prior to fuming to dryness under a nitrogen sweep. The drying procedure eliminates any potential chloride, fluoride, and volatile organic compound impurities. The presence of H_2SO_4 in the fumed solutions prevents the formation of insoluble oxides by stabilising U as soluble sulfate crystals.

To perform the electrochemical analyses, the solids thus created were redissolved in an electrolyte containing 30 mL of H_2SO_4 (0.5 mol L^{-1}) with a pH of 2.9 (adjusted through the addition of NaOH).

3.2.2. Sample analysis

The prepared samples were studied through an electrochemical procedure involving three main steps; electrode activation, blank measurement, and determination of U content.

In order to remove oxygen from the system, a stream of argon − humidified by a bubbler containing de-ionised water placed upstream from the electrochemical cell − was passed over the surface of the solution prior to the reduction during at least 15 min [17], this stream and was maintained during the experiments.

3.2.3. Electrode Pretreatment

In order to remove any surface-adsorbed O_2 or H_2, the BDD electrodes were immersed in the electrolyte (30 ml of H_2SO_4, 0.5 mol L^{-1} with a pH of 2.9 adjusted through the addition of NaOH) and subject to a series of four galvanic pulses (+1.5 V/MSE for 10 seconds followed by -1.5 V/MSE for 10 seconds).

3.2.4. Blank Measurement

Following the pretreatment procedure, a new electrolyte sample was prepared (30 ml of H_2SO_4, 0.5 mol L^{-1} with a pH of 2.9 adjusted through the addition of NaOH) and the response of the electrode to the electrolyte (the blank) was measured. Blank measurements were performed through a two stage process wherein a fixed potential of -300 mV/MSE was applied until a current of +50 µA was measured, a second potential of -1000 mV/MSE was then applied until a stable current of -50 µA was recorded. The time required to reach both current limits as well as the charge employed in each stage, were monitored with the two step procedure being repeated until reproducibility was observed.

The charge measured during the last oxidation potential step (-1000 mV/MSE) was recorded and used as the blank measurement, Q_b, during the determination of U amount content in the studied samples.

3.2.5. U content measurement

The solution used for the measurement of the blank was transferred quantitatively into a coulometric cell containing the previously prepared dry sample to be analysed (section 3.2.1). The created solution was stirred for 30 minutes in order to ensure the complete dissolution of any solid residues and then its U content was analysed by applying a fixed potential (-1000 mV/MSE) to the solution and monitoring the current employed over time until a limit of -50 µA was reached.

The time taken to reach the current limit (t_s) as well as the charge employed (Q_s) were recorded and used to determine the amount content of U in the analysed solutions as described in section 4.2.

4. Results and Analysis
4.1. Voltammetry experiments
4.1.1. Electrochemical response of BDD electrodes in the aqueous sulfate medium

The electrochemical response, as observed through cyclic voltammetry, of the BDD WE in the blank H_2SO_4 medium is presented in Figure 1.
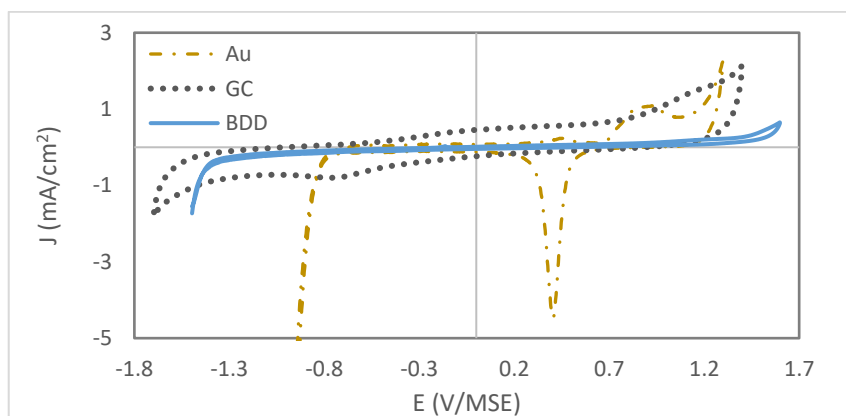

Figure 1 – Cyclic voltammograms of gold (Au), boron doped diamond (BDD), and glassy carbon (GC) disc electrodes in an aqueous H_2SO_4 medium (0.5 mol L^{-1}, pH = 0.5) measured at a scan rate of 250 mV s^{-1}.

Figure 1 compares the cyclic voltammograms of BDD to those of GC and Au in an aqueous H_2SO_4 solution (0.5 mol L^{-1}, pH = 0.5) measured at a scan rate of 250 mV s^{-1}. It is possible to see not only that the three different materials show different responses to the medium (notably the Au electrode shows a series of oxidation and reduction peaks at E > 1.1 V /SCE which are well known in scientific literature [18]) but also that each material possesses a different electrochemical window (the potential range wherein the electrodes can operate before electrolysing a given solvent [13]). By defining boundary conditions for the electrochemical window (-1 $\leq$ j $\leq$ 0.7 mA cm^{-2}) it was possible to compare the electrochemical windows of the materials numerically such that Au was seen to have the smallest window (2.0 $\pm$ 0.1 V) whilst BDD and GC had windows of comparable size (3.1 $\pm$ 0.1 V and 3.0 $\pm$ 0.1 V respectively). The similarity of the electrochemical windows of BDD and GC is in accordance with previous literature reports [12], [13] and can be attributed to the carbonaceous nature of the two materials.

The final feature that is visible in Figure 3 is the difference in capacitance for the three studied materials. Indeed the GC electrode displays a significantly wider curve than those of the Au and BDD electrodes. In cyclic voltammetry (CV) studies, the double layer capacitance C_{dl} of an electrode of geometric surface area A can be related to the current - averaged between the forward and reverse CV sweeps - i_{av}, measured at a potential where no electrochemical reaction is taking place, and the scan rate, v, of the experiment as shown in equation (2) [13].

$$C_{dl} = \frac{i_{av}}{v\,A} \qquad (2)$$

By using equation (2), it was possible to calculate the double layer capacitance for the three materials studied. In H_2SO_4 the BDD electrode displayed a capacitance of 25 $\pm$ 3 µF cm^{-2} which was consistent with that previously reported in literature for BDD electrodes in a 0.1 mol L^{-1} KNO_3 medium [14]. The experimentally determined capacitances of the Au and GC electrodes (288 $\pm$ 10 µF cm^{-2} and 946 $\pm$ 204 µF cm^{-2}, respectively) are considerably higher. However, it is worth noting that the experimentally measured capacitance for the Au electrode is much higher than that previously reported in literature under

similar conditions of 60 – 70 μF cm^{-2}, [19] indicating that the studied electrode may not have been sufficiently polished prior to experimentation. Nonetheless, the large electrochemical window and low capacitance of BDD in the studied medium provide it with the most promising profile amongst the three different WE materials for the analysis of U amount content through CPC.

4.1.2. Uranyl electrochemical behaviour in aqueous sulfate medium at BDD electrode

The interaction of BDD with uranyl ions in aqueous sulfate solutions was studied through cyclic voltammetry to determine the material's suitability for CPC. The results studies are presented in figure 2.
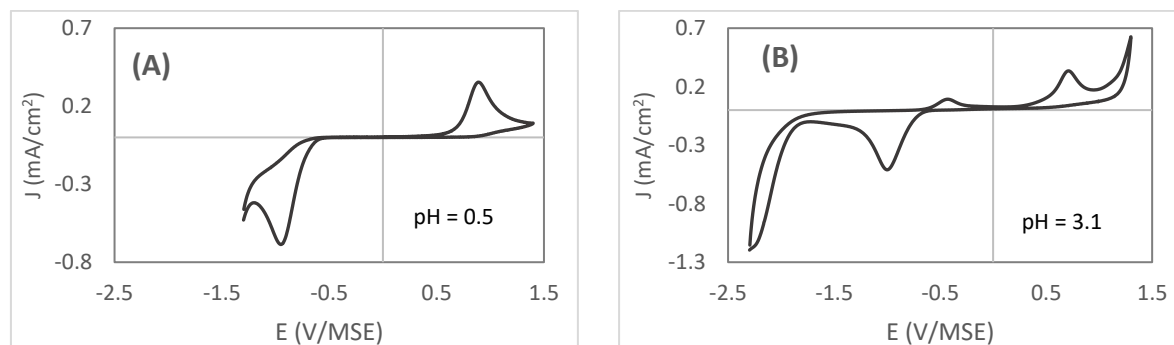

Figure 2 –*Cyclic voltammograms of the EQRAIN U 16 standard solution in aqueous H_2SO_4 media (0.5 mol L^{-1}) at pH levels of 0.5 (figure A) and 3.1 (figure (B) measured at a scan rate of 25 mV s^{-1}using a BDD working electrode. The concentration of U in the solutions is calculated to be 20 mmol L^{-1}.*

Figure 2 shows the voltammograms (ν = 25 mV s^{-1}) of the standard U solutions ([U] = 20 mmol L^{-1}) in H_2SO_4 (0.5 mol L^{-1}) at a pH levels of 0.5 (figure 2A) and 3.1 (figure 2B), recorded using a BDD WE. Two redox peaks can be observed in figure 2A, and three peaks can be observed in figure 2B, these correspond to the reactions underlying the two electron conversion between the UO_2^{2+} and U^{4+} ions at different pH levels. These peaks could be identified through correlation with previous literature studies [20], [21].

The oxidation peak visible in figure 2A at an applied potential of 0.900 mV / MSE and in figure 2B at 0.724 V/MSE can be attributed to the two electron oxidation of U^{4+} to UO_2^{2+} shown in equation (3).

$$U^{4+} + 2 H_2O \rightarrow 4H^+ + UO_2^{2+} + 2 e^- \qquad (3)$$

The reduction peak (-0.920 V/MSE and -0.990 V/MSE in Figures 2A and 2B,respectively), for its part, was interpreted according to literature as a combination of a single electron reduction of UO_2^{2+} to UO_2^{2+} (equation (4)) followed by the acid-catalysed disproportionation reaction of UO_2^+ to U^{4+} and UO_2^{2+}, better known as the E-DISP mechanism (equation (5)).

$$UO_2^{2+} + e^- \rightarrow UO_2^+ \qquad (4)$$

$$2 UO_2^+ + 4H^+ \rightarrow U^{4+} + UO_2^{2+} + 2 H_2O \qquad (5)$$
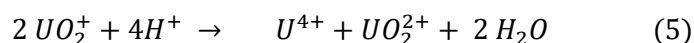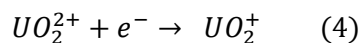
The third peak, (-0.425 V/MSE in Figure 2B), can be attributed to the oxidation of the intermediate UO_2^+ species into UO_2^{2+} as shown in equation (5). This peak is only present in the voltammogram in figure 2B as UO_2^+, whilst unstable at low pH levels, is partially stabilised at higher pH levels [22].

From these observations it is clear that in order to perform the CPC analysis of the U amount content of solutions through the reduction of the uranyl cation with BDD electrodes, a suitably negative potential must be chosen. For the present experiments, a potential of -1.0 V/MSE was deemed appropriate to ensure a quantitative reduction of the uranyl cation.

Finally, it is important to note in figure 2 that in H_2SO_4 solutions with an unadjusted pH (pH = 0.5, figure 2A) the electrochemical window's solvent wall (arising from the Hydrogen Evolution Reaction – HER)

interferes with the peak corresponding to the reduction of the uranyl cation, inducing a distortion into the recorded voltammogram. This effect is particularly important in terms of CPC analysis as it increases the proportion the blank's contribution to the total charge recorded during experiments, effectively leading to an increase in CPC measurement uncertainty. This interference can be reduced by changing the pH of the electrolyte solution, as seen in figure 2B. Indeed, it is known that the potential at which the HER occurs is related to the pH of a studied electrolyte solution [23]. As such, by shifting the studied solution's pH level to around 3 in the present experiments, it was possible to impart a negative shift on the onset potential for the HER whilst leaving the studied species (the uranyl cation) relatively unaffected.

From the results of the cyclic voltammetry studies, it was decided that CPC analyses of U solutions through BDD electrodes should be performed by studying the reduction of the UO_2^{2+} ion at a potential of -1V/MSE in an aqueous sulfate solution with a pH close to 3. Following the previously reported CPC analyses of Pu [5], [6] as well as the need to optimise practical experimental constraints (analysis time), the amount of analyte to be studied was set at a mass of 3 mg of U.

4.2. Coulometric studies

The results of the coulometric analyses performed in sulphuric media at a pH of 2.9 by applying a reduction potential of -1.0 V/MSE are shown in table 1.

To determine the U content of the studied solutions, the charge measured during the analysis of the samples, Q_s, was corrected to take into account the fraction of that charge originating from the interaction of the electrolyte and the electrodes, Q_b. This correction, performed as shown in as shown in equation (6), yielded the effective charge used for the conversion of the U in solution, Q_U,

$$Q_U = Q_s - Q_b \qquad (6)$$

The mass of U converted during the electrochemical process (m_{exp}) was then determined from Q_U by applying faraday's law (equation (1)) where $n = 2$. By taking into account the initial solution's dilution factors, it was possible to use m_{exp} to calculate an experimental estimate for the initial uranium amount content of the original standard solution, $[U]_{exp}$.

Table 1 – *Results of the CPC analyses of U performed by using BDD electrodes for samples GC39 – GC42.*

	Q_u *(mC)*	mU_{exp} *(mg)*	$[U]_{exp}$ *(g kg^{-1})*	$[U]_{ref}$ *(g kg^{-1})*	*Bias (%)*
GC39	2411.4	2.97	249.9	249.70	-0.1
GC40	2404.8	2.97	248.3	249.70	0.6
GC41	2455.3	3.03	252.7	249.70	-1.2
GC42	2412.3	2.98	246.4	249.70	1.3
Mean $[U]_{exp}$ (g kg^{-1})			249.3	Mean Bias (%)	0.2
St. dev (g kg^{-1})			2.7		
RSD (%)			1.1		

The repeatability of CPC for the determination of U amount content in the experimental conditions hitherto outlined is reported in table 1. Indeed, the four $[U]_{exp}$ values were calculated to have a standard deviation of 2.7 g kg^{-1}, (1.1% in relative terms).

By taking the arithmetic mean of the four $[U]_{exp}$ values and estimating its uncertainty through the uncertainty propagation methods outlined in the GUM [24] the expression of the final results for the CPC analysis of U is:

$$[U]_{exp} = (249.3 \pm 4.6) \text{ g kg}^{-1} \text{ (k=2)}$$

This final result was used to determine the method's trueness by analysing the significance of the method's bias relative to the certified U amount content of the reference solution through the normalised deviation

term, E_n, expressed as shown in equation (7) where $[U]_{exp} = 249.3$ g kg^{-1}, $u_{exp} = 2.3$ g kg^{-1}, $[U]_{ref} = 249.70$ g kg^{-1}, and $u_{ref} = 0.125$ g kg^{-1}.

$$E_n = \frac{[U]_{exp} - [U]_{ref}}{\sqrt{u_{exp}^2 + u_{ref}^2}} \qquad (7)$$

In equation (7) if E_n is inferior to 2 in absolute terms, then the bias between the two studied values is statistically non-significant. For the present experiment $E_n = -0.73$, indicating that CPC can be considered a true method for the analysis of U amount content in aqueous sulfate solutions with BDD electrodes.

5. Conclusions

The present paper outlined the work carried out by the CETAMA towards the application BDD as an alternative electrode material to Hg for the analysis of the U amount content of solutions through CPC.

Initial cyclic voltammetry studies showed that BDD electrodes displayed a large electrochemical window (3.1 ± 0.1 V) as well as a small double layer capacitance (25 ± 3 µF cm^{-2}) which allow to study the electrochemical properties of the $U^{VI/IV}$ redox couple. However, it was also observed that at a pH of 0.5 a significant interference from the interaction of the BDD and the electrolyte medium existed due to the proximity the BDD working electrode's solvent wall to the reduction potential of UO_2^{2+}. This interference was reduced by changing the pH of the electrolyte medium such that the onset potential of the HER was shifted negatively. From these studies, it was determined that the CPC analyses of U amount content in sulfate solutions should be performed by studying the reduction of the UO_2^{2+} cation at an applied potential of -1 V/MSE in solutions with a pH of 2.9.

Consequently, BDD electrodes were used to analyse the U amount content of sulfate solutions through CPC. A relative standard deviation of 1.1% was seen between the results of four independent analyses, showing that the technique could be applied with a repeatability comparable to that of previous CPC analyses of U using Hg electrodes in similar media [25], [26]. Furthermore, from statistical analysis it was possible to determine that no significant bias existed between the final experimentally determined U amount content, for whom an expanded relative uncertainty of 1.84% was calculated, and the analyte's certified U amount content.

Ultimately, whilst these coulometric results are still far from the levels of trueness reached by for the CPC analyses of Pu [8], it is not inconceivable that such performances may be attained with further optimisation. Indeed, as the present experiment sought to demonstrate the applicability of BDD to the CPC analysis of U, no optimisation effort was made. As such, a number of avenues (electrode geometry and surface area, studied mass of analyte, electrolyte pH, applied reduction potential …) remain to be pursued in the quest to lower the technique's analytical uncertainties. Attaining such uncertainties would represent a significant advancement for CPC as, due to BDD's unique properties, the technique could become routinely used not only for the analyses U but also for those of a large variety of other actinides.

6. References

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