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Original Article

Effects of Inert Gas Sparging Deaeration Method on Zirconium Analysis in Aqueous Media

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Abstract - *This study evaluates the impact of the inert gas (N_2, Ar) bubbling deaeration method on the electrochemical analysis of zirconium in alkaline aqueous media. Nitrogen, tested with flow rates of up to 10 cm³/s and prolonged bubbling times (1 h), was seen to be ineffective in suppressing interferences related to the reduction of residual oxygen (peak at -1.1 V/SCE), systematically masking the Zr (IV) signal. In contrast, argon allowed an optimal removal of dissolved O_2, revealing a clear reduction of Zr (IV) to Zr (0) from -1.5 V/SCE, with a current density proportional to the zirconium concentration (7 to 18 mA/cm² for 0.001 to 0.005 M). Parameter optimization (Ar flow rate: 5 cm³/s; time: 30 min) improved the reproducibility and sensitivity of the measurements, eliminating electrochemical artifacts. These results reveal the effectiveness of argon for analyses in oxygenated environments, providing a reliable method for the precise quantification of zirconium, particularly in critical industrial contexts such as nuclear power. This approach now opens up prospects for adaptation to other electrochemical systems sensitive to dissolved gases.*

Keywords - *Argon, Bubbling deaeration, Electrochemical analysis, Nitrogen, Zirconium.*

1. Introduction

Zirconium (Zr), a transition metal of group 4 with atomic number 40, was first identified in 1789 by Martin Heinrich Klaproth in zircon (zirconium orthosilicate) and later isolated in metallic form by Jöns Jacob Berzelius in 1824[1][2]. It possesses exceptional physicochemical properties, including multiple oxidation states (+4, +3, +2, 0, −2), a high melting point (1852 °C), remarkable corrosion resistance, and very low neutron absorption cross-sections [3][4]. These attributes make zirconium indispensable in strategic industries, particularly nuclear power, where it is widely used as cladding material in fuel rods and in reactor components [5][6]. A central feature of zirconium chemistry is its strong affinity for oxygen, which leads to the formation of a stable protective oxide layer (ZrO_2) at both ambient and elevated temperatures. The electrochemical analysis of zirconium has a particular sensitivity that can be linked to the presence of gas dissolved in the solution, in this case oxygen, which has a very strong affinity with zirconium [7]. This affinity of Zirconium for oxygen was confirmed by Benoît MAZARES during his research work entitled "Experimental study and modeling of oxidation and associated phase transformations in Zirconium alloy cladding". According to the authors, zirconium exhibits high chemical reactivity with oxygen at room temperature, conferring great stability to the oxide formed [8]. A. A. Aleksandrov et al. have worked on the thermodynamics of oxygen solutions in the molten zirconium-containing Fe-Co system. They proved that Zr(s) reacts with O_2(g) to form ZrO_2(s); thereby demonstrating the strong affinity of zirconium for oxygen, which results in the formation of a protective oxide layer when exposed to oxygen. This oxide layer, usually zirconium dioxide (ZrO_2), provides excellent corrosion resistance [9].

This theory has been confirmed by the same authors in another study relating to oxygen solubility in zirconium-containing Ni–Co melts. They performed a thermodynamic analysis of oxygen solutions in zirconium containing Ni-Co and determined the interaction of zirconium with oxygen in Ni-Co melts [10]. While this property confers excellent corrosion resistance, it poses unique challenges for electrochemical studies and analytical determinations of zirconium in aqueous systems. The dissolved oxygen present in solutions not only competes with zirconium reduction ($E° O_2/H_2O = 1.229$ V vs. SHE, $E° Zr^{4+}/Zr = -1.539$ V vs. SHE) [11], but also generates additional peaks in voltammograms, complicating the accurate quantification of zirconium. This was demonstrated by E. Ortiz Ortega et al. in their studies on characterization techniques for electrochemical analysis. They examine in detail the mechanisms of oxygen reduction on different electrode surfaces and the associated reaction products. They also discussed challenges related to electrochemical detection in the presence of dissolved oxygen [12]. In addition, R. Sehrawat et al. have studied the "Effect of solvents on electrochemical performance of polypyrrole coated LiFePO4/C cathode materials for Li-ion

battery''; they explored how dissolved oxygen affects electrochemical reactions on metal electrodes, particularly in terms of oxide layer formation and interference with other electrochemical processes [13]. This interference highlights the necessity of reliable deaeration methods to remove oxygen prior to electrochemical measurements [14].

Various deaeration strategies have been reported across different fields, including vacuum-based techniques [15][16], chemical deaeration [17], inert gas sparging [18][19], and bioelectrochemical systems [20]. Among these, vacuum deaeration is often considered efficient for oxygen removal; however, its reliance on vacuum pumps and heat exchangers renders it technically complex and economically burdensome, particularly for small-scale applications. This limitation was highlighted by Yong-Du Jun et al. in their study "Degassing Dissolved Oxygen through Bubbling: The Contribution and Control of Vapor Bubbles" [21], where the authors emphasized that although vacuum systems achieve effective gas elimination, the required infrastructure and associated heat management significantly increase operational and maintenance costs. With regard to chemical deaeration, this approach requires the handling and storage of reagents, which raises both safety and environmental concerns. In addition, the introduction of external chemicals may contaminate the medium, potentially compromising the efficiency of the process and the reliability of the results. X. Liu et al., in their analysis of oxygenated treatment practices in a 350 MW supercritical unit using desalted feedwater, reported that maintaining the proper treatment conditions necessitates continuous monitoring, which increases operational complexity and costs [22]. Complementarily, S. Benyahia et al., in their work "Numerical study of deaeration of aeratable particles" [23], highlighted the possibility of undesirable chemical by-products that may adversely affect the quality of the processed material. Considering these factors, inert gas sparging emerges as a particularly suitable approach for the present study. This technique offers straightforward control and can be readily adapted to different process scales. Its main advantages include efficient oxygen removal, preservation of a non-oxidizing environment, operational simplicity, absence of chemical contamination, the ability to regulate temperature, scalability, dual functionality, and rapid mass transfer kinetics [24][25][26].

Despite these advantages, a clear research gap remains: although gas sparging has been studied in various fields, its systematic impact on the accuracy, sensitivity, and reproducibility of zirconium analysis in aqueous media has not been thoroughly evaluated. Specifically, the influence of sparging parameters such as gas type, sparging time, and gas volume on the precision and reliability of zirconium quantification has not yet been critically examined.

Some others have worked on the gas sparging method, but did not systematically evaluate the inert gas sparging method to improve the accuracy, sensitivity, and reproducibility of zirconium quantification. Indeed, Consiglio et al. [27] advanced molten salt electrochemistry by designing a high-temperature, glovebox-compatible cell to probe hydrogen behaviour in FLiBe; their focus was on engineering challenges of cell design and operation. They investigate the diffusivity of hydrogen in FLiBe using the electrochemical cell to conduct linear sweep voltammetry. It should be noted that hydrogen, not an inert gas, will likely interfere in the process. Hassan et al. [28] have demonstrated that inert gas sparging in rotating cylinder electrochemical reactors enhances mass transfer and improves energy utilization efficiency, with applications in wastewater treatment, hydrogen peroxide production, and flue gas desulphurization. Their work, however, remained focused on reactor-scale process intensification. In contrast, the present study introduces a novel application of inert gas sparging in analytical electrochemistry, specifically for the quantitative determination of zirconium in aqueous and organic media. Sparging is not employed here to boost bulk reaction rates but to suppress oxygen interference, stabilize the electrochemical environment, and improve analytical precision.

The novelty of this work lies in providing the first comparative, parameter-driven evaluation of inert gas sparging for zirconium analysis, bridging the gap between general deaeration practices and their specific analytical consequences. Addressing this gap is crucial for establishing standardized and optimized protocols that ensure high-quality zirconium measurements, particularly in nuclear and electrochemical applications where precision is essential.

The principal aim of this article is to critically evaluate the impact of inert gas sparging on the precision, accuracy, and overall effectiveness of zirconium analysis in aqueous media. Some specific goals have been defined to achieve this aim. These involve, among other things:

- ✓ Comparing the analytical results of zirconium quantification with and without the use of inert gas;
- ✓ Comparing the effects of different gases (e.g., nitrogen, argon) used during deaeration on the precision and accuracy of zirconium measurements;
- ✓ Analysing the influence of deaeration time on the effectiveness of oxygen removal and its subsequent impact on zirconium analysis;
- ✓ Evaluating the role of gas volume in achieving optimal deaeration conditions and its effect on minimizing interferences during zirconium analysis;
- ✓ Determining the combined impact of these variables (time, gas type, and volume) on the sensitivity and reproducibility of zirconium quantification in aqueous media in order to propose optimal deaeration conditions for improving the quality and reliability of zirconium analysis across diverse experimental environments.

By filling this gap, the study seeks to establish optimal deaeration conditions for enhancing the reliability of zirconium electrochemical analysis across diverse experimental environments.

2. Experimental Part

2.1. Chemical Products

This study exclusively employed analytical-grade reagents to guarantee high experimental reliability. To ensure the highest data fidelity, all experiments utilized reagents of analytical grade, sourced from Sigma-Aldrich. The study employed concentrated nitric acid (68% HNO_3) and hydrochloric acid (37% HCl) as components of the dissolution medium. Zirconium standard solutions (0.1 M and 0.01 M) were used for calibration. High-purity nitrogen and argon gases, essential for the deaeration experiments, were supplied by Air Liquide. The zirconium ore sample analysed was sourced from Senegal's titaniferous sand mines, operated by Grande Côte Operations (GCO), which is part of the ERAMET group. The experimental work was conducted at the Laboratory of Chemical Engineering, University Paul Sabatier, Toulouse III, France.

2.2. Experimental Device

Electrochemical measurements were performed in a Metrohm-type three-electrode cell (100 cm^3 volume). A glassy carbon disk electrode served as the working electrode and was systematically polished prior to each experiment using a MECATECH 234 REF. 67100 polisher equipped with 200 - 250 mm diameter plates and TC10, TI10, and TCI10 polishing heads to ensure optimal surface preparation [29]. The reference electrode was a saturated calomel electrode inserted into a salt bridge to minimize cross-contamination. A platinum wire was employed as the counter electrode. The cell was equipped with a magnetic stirrer, and the setup was connected to an Origalys OGS100 potentiostat-galvanostat interfaced with ORIGA MASTER software for voltammogram recording. For gas supply, a tube connected to nitrogen or argon cylinders was immersed in the electrochemical cell.

2.3. Experimental Procedure

The composition of the zirconium ore sample was determined beforehand using X-Ray Fluorescence (XRF) analysis. (see Table 1)

Table 1. Zircon powder composition obtained by X-Ray Fluorescence (XRF)

XRF ANALYSES OF ZIRCON (Values expressed in %)						
Oxide	**TiO_2**	**ZrO_2**	**CaO**	**Fe_2O_3**	**Al_2O_3**	**SiO_2**
%	0.11	**67.01**	0.03	0.07	0.26	32.52

The zirconium sample was dissolved via a process that will not be described in this article; Studies were carried out in an alkaline medium. The procedures for studying the effect of the inert gas sparging deaeration method on zirconium analysis in alkaline media are described below.

A defined volume of zirconium solution, obtained by dissolving zircon powder in aqua regia, was transferred into 10 cm^3 of the selected solvent/electrolyte. The electrochemical cell (20 cm^3) contained this solution, in which three electrodes connected to a potentiostat were immersed. For experiments in alkaline medium, the pH was adjusted to 13 by the gradual addition of saturated NaOH solution, and the final volume of the prepared electrolyte was fixed at 15 cm^3. A glass carbon electrode was used as a working electrode. To avoid disturbances on the curve $I = f(E)$, due to dissolved oxygen reduction, the *inert gas sparging deaeration method* was used to maintain an inert atmosphere within the electrochemical cell.

Figure 1 presents the overall setup used to study the effect of inert gas sparging on the electrochemical analyses of Zirconium in aqueous media.

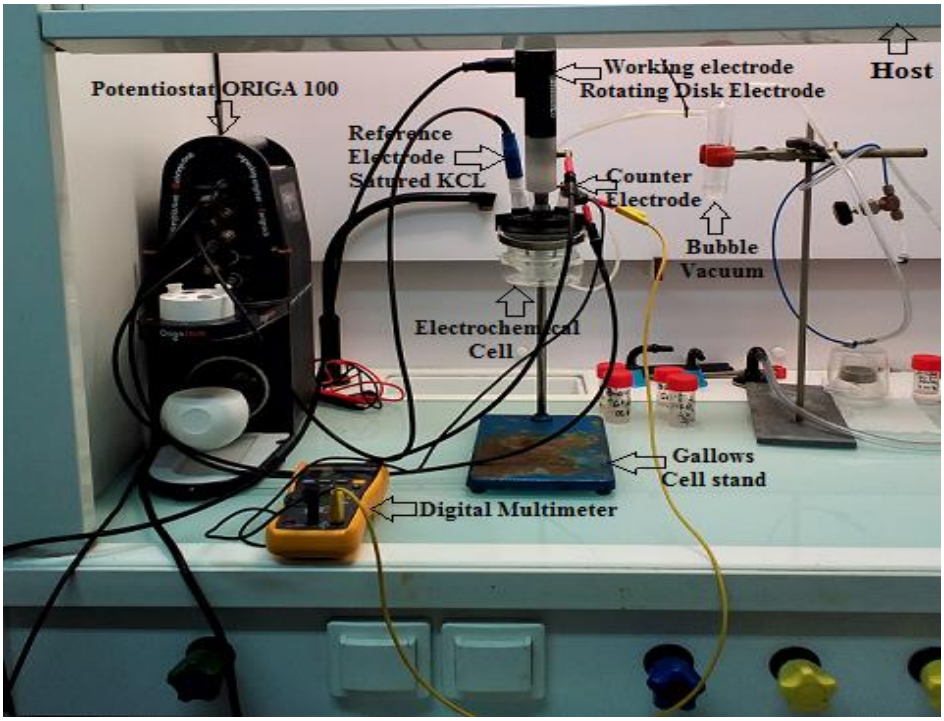

Fig. 1 Experimental set-up used for studying the impact of inert gas sparging on the electrochemical analyses of zirconium solutions.

3. Results and Discussion

3.1. Effect of Inert Gas Sparging in Electrochemical Analysis of Zirconium in an Aqueous Medium

Different electrochemical results obtained during the electrochemical analyses of zirconium in an aqueous medium, under different operating conditions, are presented in this section. Emphasis is placed on the effect of nitrogen and argon gas in this electrochemical examination of zirconium in an alkaline medium. The effects of nitrogen and argon gases were studied with the aim of potentially removing the oxygen in the solution in order to extend the solvent electrochemical window. Initially, the first part of this study was made with three solutions of commercial zirconium of known concentration. Later in the second part of the studies, the focus was placed on the zirconium sample, which is produced at the Grande Côte Operations (GCO) mine in Senegal.

3.2. Reduction of Commercial Zirconium Solutions in an Alkaline Medium: the effect of Nitrogen Bubbling

Electrochemical reduction experiments were performed by recording current-potential $I = f(E)$ curves on a rotating glassy carbon electrode in a strongly alkaline medium (pH 12-13), obtained by the addition of saturated sodium hydroxide. Three commercial zirconium solutions were examined (S', S'', and S'') with molar concentrations of 0.001, 0.003, and 0.005 M, respectively. Prior to data acquisition, the electrolyte was deaerated through continuous nitrogen sparging at a flow rate of 1 cm^3/s for 15 minutes to ensure complete removal of dissolved oxygen. The results are presented in Figure 2 below.

No reduction signal attributable to zirconium was detected. The recorded waves were instead associated with the reduction of residual dissolved oxygen, which had not been completely removed by nitrogen purging. This process occurred at around 200 mV, a relatively low potential, thereby suppressing any possible reduction of zirconium in solution. Under the applied experimental conditions, the effect of nitrogen proved negligible. In order to improve the efficiency of nitrogen gas in oxygen removal in solution, the nitrogen flow rate was then increased from $1cm^3/s$ to $5cm^3/s$, while the sparging time was also extended from 15min to 30 min.

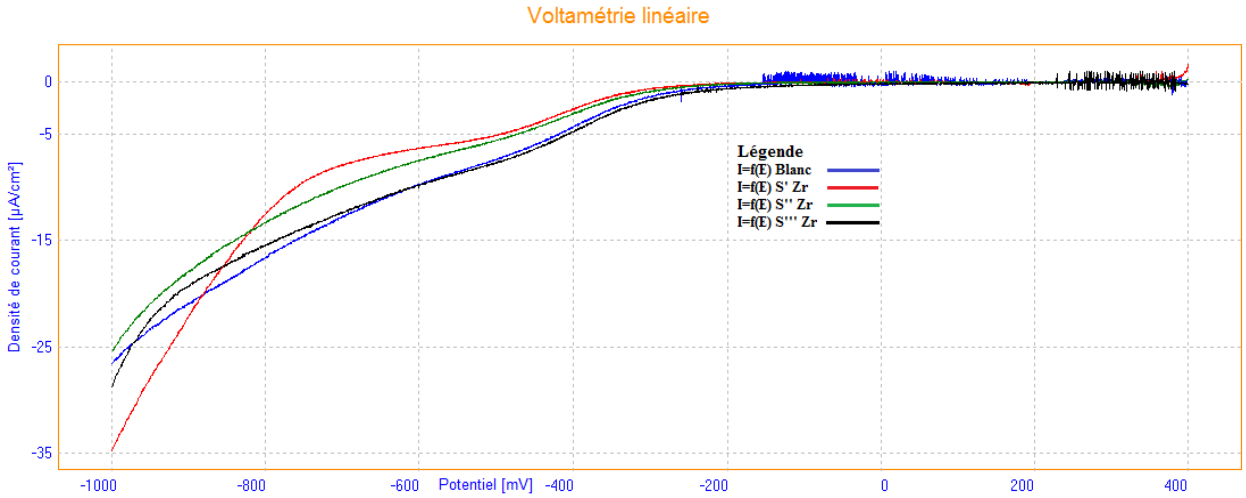

Fig. 2 Curves I=f(E) in reduction on a rotating glassy carbon disk, d=3 mm, immersed in the blanc, then in 3 Zr solutions S' = 0.001 M, S'' = 0.003 M, S''' = 0.005 M; Bubbling gas N_2: 15 min, nitrogen flow rate $1cm^3/s$; ω = 1000rpm, r=20mV/s, E.Aux: Pt, E.Ref: SCE.

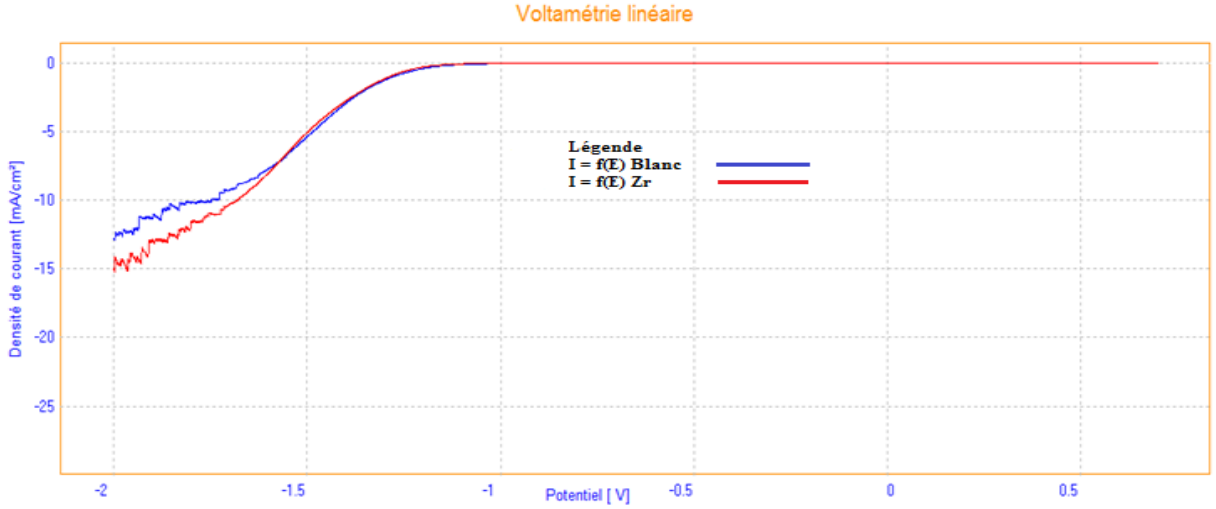

Fig. 3 Curve I = f (E) in reduction on a rotating glassy carbon disk, d = 3 mm, immersed in the blank and in a second solution of Zr 0.001 M; Bubbling gas N_2: 30 min, nitrogen flow rate $5cm^3/s$; ω = 1000 rpm, r=20 mV/s, E.Aux: Pt, E.Ref: SCE.

3.3. Reduction of Commercial Zirconium Solution in an Alkaline Medium: The Effect of Nitrogen Sparging Time and Flow Rate

In the continuation of this study relating to the nitrogen bubbling effect in zirconium reduction in an alkaline medium, a commercial zirconium solution was analysed for reduction on a rotating glassy carbon disk. In this case, the nitrogen flow rate was increased from 1cm^3/s to 5cm^3/s, and the sparging time was extended from 15 min to 30 min.
The concentration of zirconium in the solution was first determined by ICP analysis.

The ICP analysis revealed the following mass concentration: $C_{m\ zirconium} = 0.5g/dm^3$.

Figure 3 above shows the profile of the potential intensity curves obtained in reduction on a rotating glassy carbon disk.

Despite the increase in the bubbling time and the flow rate, no zirconium signal was observed. The reduction wave that appears on the two voltammograms from -1.1V still corresponds to the reduction of dissolved oxygen. However, compared to graph number 2, the oxygen reduction potential has been extended thanks to the increase in the bubbling time and the increase in the nitrogen flow rate. Taking into consideration these two experiments' results, it can easily be deduced that the use of N_2 as a bubbling gas does not automatically lead to a significant decrease in dissolved oxygen; therefore, it does not promote the reduction of zirconium in solution.

Several experiments were carried out by gradually increasing the flow rate up to *10 cm^3/s*; as for the bubbling time, it was raised to *1h*. Nevertheless, no zirconium signal was observed. The objective was not achieved with the use of nitrogen as deaeration gas; in the remainder of the experiment, argon was used as a bubbling gas in order to detect the zirconium signal. Studies show that argon is 2.5 times more soluble in water than nitrogen (approximately the same solubility as oxygen).

This is because heavier gases tend to be more soluble at constant temperature. In this case, argon (39.95 g/mol) was found to be more soluble than nitrogen (28.01 g/mol) [30].

3.4. Reduction of Commercial Zirconium Solution in an Alkaline Medium: The Effect of Argon bubbling

This section studies focused on the ability of argon to displace dissolved oxygen in solution in order to promote the detection of zirconium. The process remains the same; argon was introduced into the solution through a device connected to an argon gas cylinder. A pressure gauge was used to regulate the volume flow of argon gas and thus determine the volume of argon introduced into the solution in a well-defined time.

The results are presented in Figure 4.

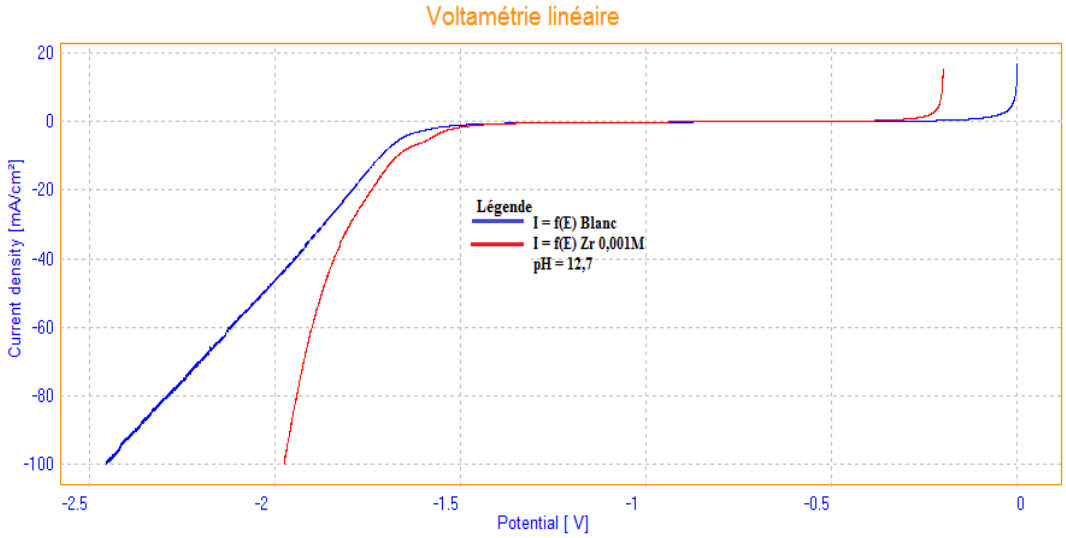

Fig. 4 Curve I = f (E) in reduction on a rotating glassy carbon disk, d = 3 mm, immersed in a solution without Zr and in a second solution of $Zr^{(IV)}$ 0.001M, alkalized to pH between 12 and 13 with saturated NaOH; Bubbling gas Ar: 15 min, argon flow rate 1cm^3/s, ω = 1000 rpm, r = 20 mV/s, E. Aux: Pt, E. Ref: SCE.

The use of argon gas helped to overcome one of the major obstacles to the electrochemical detection of zirconium, namely the interference caused by dissolved oxygen.

The use of argon gas caused a wave to appear from -1.5 V/SCE, corresponding to the reduction of Zirconium (IV) to Zr (0), the current density amounting to about 7 mA/cm^2.

Based on the Pourbaix diagram, zirconium, present as $HZrO_3^-$ in an alkaline medium, it is reduced to metallic Zr (0) at around -1.5 V. The reaction is as follows:

$$HZrO_3^- + 5H^+ + 4e^- \leftrightarrow Zr(s) + 3H_2O$$

These results lead to the following conclusion: *the appearance of the zirconium reduction wave was boosted by the medium, which was poor in oxygen gas*.

Indeed, the introduction of argon gas was found to contribute to the progressive elimination of dissolved oxygen by a degassing mechanism. This process was based on the displacement of dissolved oxygen by argon, which was injected through the solution at a controlled flow rate. By decreasing the concentration of dissolved oxygen, the parasitic contributions of the latter in the electrochemical response became negligible. In fact, argon sparging removes dissolved oxygen mainly through a physical stripping process. When argon bubbles pass through the solution, oxygen diffuses into them due to the concentration gradient at the gas-liquid interface, after which it is carried away as the bubbles escape. This continuous renewal of the interface, combined with enhanced convection and mixing, accelerates oxygen transfer from the liquid to the gas phase. Compared with nitrogen, argon provides higher efficiency because of its lower solubility and greater inertness, ensuring a stable, non-reactive environment. As a result, electrochemical interferences from oxygen reduction are eliminated, enabling clearer and more reproducible detection of zirconium reduction. After the reduction of zirconium, the solvent itself underwent reduction at approximately -1.7 V versus SCE, which marked the onset of the solvent wall.

3.5. Reduction of Commercial Zirconium Solution in an Alkaline Medium: The Effect of Argon Sparging Time and Flow Rate

In order to confirm the positive effect of argon on the electrochemical analysis of zirconium in an alkaline medium, the previously analysed commercial zirconium solution was analysed again by varying the operating conditions. For this purpose, the volume flow rate of the argon gas was increased from 1cm^3/s to 5cm^3/s and the argon bubbling time was increased from 15 min to 30 min. The operating protocol used remained unchanged. The solution was alkalized to a pH of 12.7. Intensity-potential curves were plotted in reduction on a rotating glassy carbon disk.

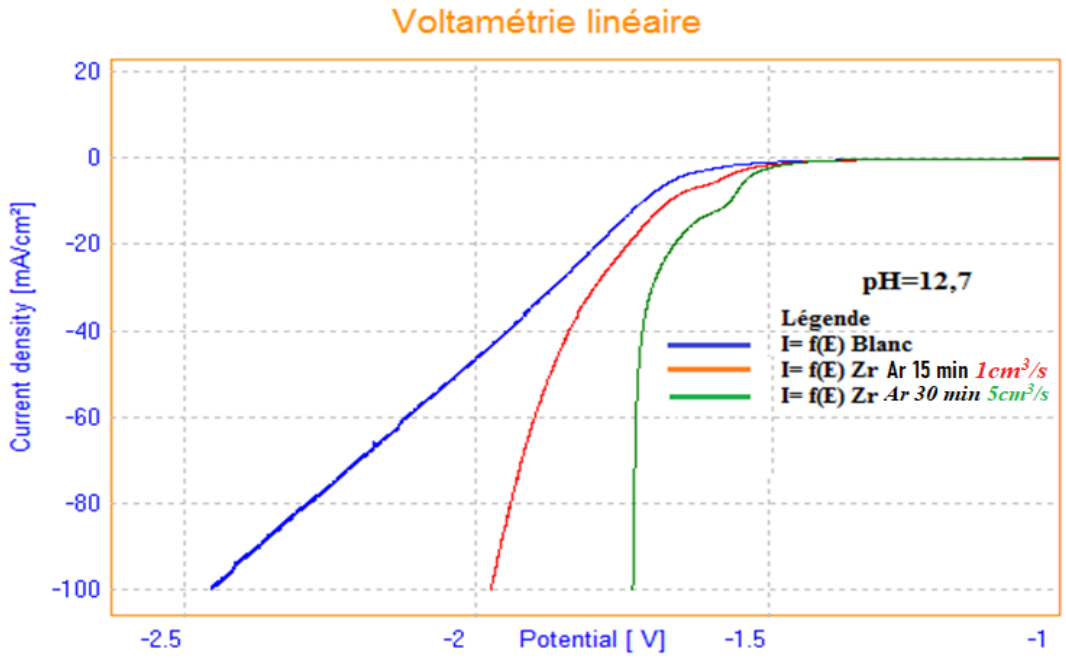

Fig. 5 Curve I = f(E) in reduction on a rotating glassy carbon disk, d = 3 mm, immersed in a NaOH solution at pH 12.7 containing commercial Zr 0.001M, alkalized to pH between 12 and 13 with saturated NaOH; bubbling gas Ar: 15 min, argon flow rate 1cm^3/s then in a the same solution, bubbling gas Ar: 30 min, argon flow rate 5cm^3/s; ω = 1000 rpm, with r = 20mV/s, E. Aux: Pt, E. Ref: SCE.

The red and green curves I = f (E) indicate reduction waves which start from -1.5 V/SCE. However, it should be noted that the amplitude of the zirconium reduction potential was particularly influenced by the volume of argon gas used during bubbling and the bubbling time. This effect of argon on the electrochemical measurement of zirconium could be observed through the red curve (*bubbling gas Ar: 15 min, argon flow rate 1cm^3/s*) and the green curve (*bubbling gas Ar: 30 min, argon flow rate 5cm^3/s*). It was then able to deduce from this study that the use of argon as a deaeration gas made it possible to minimize very considerably the interferences caused by undesirable electroactive species, in particular dissolved oxygen. Indeed, the presence of dissolved oxygen in solution was found to disturb the electrochemical measurements because dissolved oxygen is electroactive, particularly in an alkaline medium, where it is easily reduced on the surface of the electrode. This reaction generates parasitic currents that mask or disrupt zirconium-specific signals. Moreover, in an alkaline environment, oxygen reduction products, such as hydroperoxide ions, can interact with zirconium complexes, altering their electrochemical behaviour.

Furthermore, by increasing the argon volume flow rate from 1 cm³/s to 5 cm³/s and the bubbling time from 15 min to 30 min, it was possible to discharge the oxygen more efficiently, allowing better separation of zirconium-specific signals.

The elimination of interferences via argon (inert gas) allows one to identify the specific reaction mechanisms more clearly. Indeed, without effective purging, bubbles of dissolved oxygen in solution can form on the surface of the electrode, disrupting the homogeneous diffusion of electroactive species.

Argon removes these bubbles, which improves the stability of the recorded current (a clear increase in the reduction current density) and reduces fluctuations.

3.6. Reduction of zirconium solutions obtained from an ore sample from a GCO Senegal mine: the effect of argon gas in the electrochemical process

In the final phase of this study, three solutions prepared from a zirconium ore extracted from the GCO mine (Senegal) were analysed.

Three solutions were prepared to confirm the role of argon in zirconium electrochemical analysis. Initially, 0.03 g of ZrO_2 powder was dissolved in aqua regia to obtain solution S_0, whose concentration was measured by ICP as 0.001 M. From S_0, two further solutions, S_1 and S_2, were prepared and characterized by ICP, giving concentrations of 0.003 M and 0.005 M, respectively.

All solutions were adjusted to pH 13 using saturated NaOH. Reduction curves were recorded on a rotating glassy carbon disk, with argon employed as the deaeration gas under mild conditions (bubbling time: *15 min*; flow rate: *1 cm^3/s*).

The results are presented in Figure 6 below.

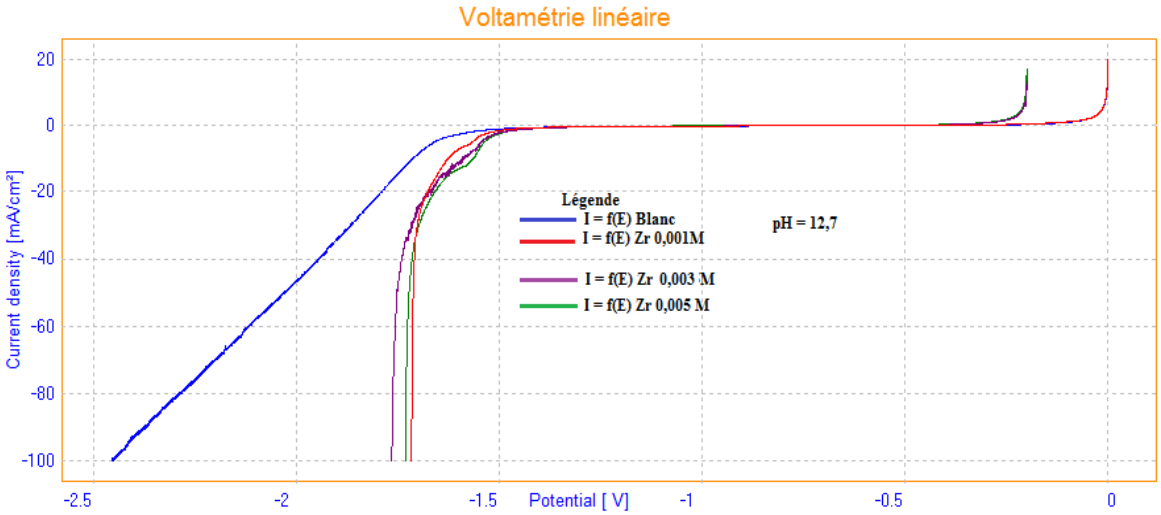

Fig. 6 Curves I = f (E) in reduction on a rotating glassy carbon disk, d = 3 mm, immersed in the blanc, then in 3 Zr solutions S_0 = 0.001 M, S_1 = 0.003 M, S_2= 0.005 M, alkalized to pH=12.7; Bubbling Ar: 15min, argon flow rate 1cm^3/s; ω = 1000 rpm, r = 20 mv/s, E. Aux: Pt, E. Ref: SCE.

All the voltammograms plotted showed a characteristic signal of zirconium from a reduction potential of -1.5 V/SCE. In addition, a notable variation in the amplitude of the reduction current density was observed, and this was proportional to the concentration of the species in solution. This linear relationship highlights the sensitivity of the electrochemical system to the zirconium concentration:

- ✓ For a zirconium solution S_0 with a molar concentration equal to 0.001M, the amplitude of the reduction current density is equal to 7 mA/cm^2 (red curve);
- ✓ For a zirconium solution S_1 with a molar concentration equal to 0.003M, the amplitude of the reduction current density is equal to 12 mA/cm^2 (purple curve);
- ✓ For a zirconium solution S_2 with a molar concentration equal to 0.005M, the amplitude of the reduction current density is equal to 18 mA/cm^2 (red curve).

These results confirm the beneficial effect of argon bubbling, which eliminates almost all traces of dissolved oxygen in the solution. It facilitated the progressive elimination of dissolved oxygen through a degassing mechanism involving the displacement of oxygen molecules by argon bubbles. This process, known as gas sparging, enhances the removal efficiency by promoting the diffusion of oxygen from the liquid phase into the gas phase, thereby reducing the dissolved oxygen concentration. By decreasing the concentration of dissolved oxygen, the parasitic contributions of the latter in the electrochemical response became negligible. The controlled flow rate of argon and the careful monitoring of the electrochemical response contributed to the reproducibility and reliability of the results.

Based on these experimental results, it can be confirmed that the technique is quantitative and allows the concentration of zirconium in solution to be determined by measuring the intensity of the reduction current. The different curves (red, purple, green) clearly show this linear relationship, which reinforces the validity of electrochemical measurements.

4. Conclusion

This study represents the first systematic and parameter-driven application of inert gas sparging for

zirconium electroanalysis. While sparging is a known deaeration method, its analytical optimization has never been explored for this metal. Most previous work applied gas sparging in reactor intensification or with non-inert gases such as hydrogen, often introducing interference. This study has demonstrated a clear advancement by identifying argon as uniquely effective compared to nitrogen for zirconium systems. It establishes that the choice and application of deaeration protocol is paramount for the successful electrochemical analysis of zirconium. We found that nitrogen, a commonly used gas, is inadequate for this purpose, failing to suppress the oxygen reduction interference even under extreme conditions; bubbling times (up to 1 h) and high flow rates (10 cm^3/s). Interferences related to the reduction of residual oxygen systematically masked the zirconium signals, making its detection impossible. In contrast, the use of argon allowed an optimal deaeration, eliminating electrochemical disturbances and clearly revealing the reduction of Zr (IV) to Zr (0) starting from -1.5 V/SCE. A linear relationship between zirconium concentration (0.001 to 0.005 M) and reduction current density (7 to 18 mA/cm^2) was established, confirming the sensitivity and reproducibility of the method. Increasing the argon flow rate (1 cm^3/s to 5 cm^3/s) and the bubbling time (15min to 30 min) significantly improved deaeration efficiency, reducing interferences and stabilizing the measurements.

These results highlight the importance of the choice of inert gas and the optimization of operating parameters (flow rate, time) for electrochemical analyses of zirconium. The proposed method, based on argon, offers a robust solution for studies in complex media, particularly in the nuclear industry, where the precision of the analyses is critical. Future work could explore the extension of this approach to other media (organic, molten salts, etc.) or to multi-electrolyte systems, as well as its integration into automated industrial processes.

The method was validated on solutions prepared from a zirconium mineral extract from the Grande Côte Operations (GCO) mines in Senegal. The measured reduction currents showed remarkable linearity with respect to zirconium concentration, confirming the method's ability to quantify this metal accurately and reproducibly. The voltammograms obtained on solutions of varying concentrations (from 0.001 M to 0.005 M) illustrated a direct correlation between current density and zirconium concentration in solution.

This study demonstrated conclusively the significant impact of the inert gas bubbling degassing method, particularly argon, on the electrochemical analysis of zirconium in aqueous (alkaline) media. The use of argon was significantly more effective than nitrogen in removing dissolved oxygen, minimizing interferences and widening the electrochemical window of the solvent.

In conclusion, this study validates argon bubbling as a preferred method for improving the reliability of electrochemical analyses of zirconium, opening up perspectives for both academic and industrial applications.

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Authors 1, 2 and 3 contributed equally to this work.

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