World Journal of Advanced Engineering Technology and Sciences
eISSN: 2582-8266
Cross Ref DOI: 10.30574/wjaets
Journal homepage: https://wjaets.com/

(RESEARCH ARTICLE)

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# OPTIMIZATION OF VOLTAMMETRIC METHODOLOGY FOR THE DETERMINATION OF ALUMINIUM IN DRINKING WATER BY COMPLEXATION WITH ALIZARIN RED S

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World Journal of Advanced Engineering Technology and Sciences, 2026, 20(02), 227–239

Publication history: Received on 01 July 2026; revised on 17 August 2026; accepted on 19 August 2026

Article DOI: https://doi.org/10.30574/wjaets.2026.20.2.0417



## ABSTRACT

The purpose of this work was to optimize, through experimental design, the differential pulse voltammetry technique using a hanging drop mercury electrode (HMDE) for the determination of Al(III) in drinking water. Since Al(III) is electrochemically inactive in the explored potential range, it cannot be easily determined by conventional voltammetry because it is difficult to reduce it in the electrode in aqueous solution, since its reduction potential is very negative and very close to the reduction potential of hydrogen. However, after the complexation reaction of the Al(III) ion and alizarin red S (ARS), an anodic voltammetric peak is obtained corresponding to the oxidation of the anthraquinone group at -1.07 V (vs Ag/AgCl) using the supporting electrolyte ammonium chloride 1.0 mol $L^{-1}$. Instrumental factors and pH were studied using the Plackett-Burman exploratory design to screen the relevant factors and then; to optimize the factor levels, a central composite design (CCD) was performed. The best voltammetric responses were obtained when pH 9,2, pulse time of 15 ms, pulse amplitude of 50 mV and scan rate of 25 mV $s^{-1}$ were used. With the optimized parameters, the current relative to the complex was linearly dependent on the Al(III) concentration in a range of 0.82 to 3.67 µg $mL^{-1}$. The relative error between the estimated and observed current was 3.97% for the average of 5 independent readings of a 4 µg $mL^{-1}$ Al(III) solution in the voltammetric cell. The detection and quantification limits were 0.25 and 0.82 µg $mL^{-1}$, respectively.

**Keywords:** Differential pulse voltammetry; Otimization; Aluminium; Alizarin red S.

## 1 INTRODUCTION

Aluminium is an element of considerable biological, environmental, and industrial importance to which human exposure is frequent; it can be widely found in the air, in water with low pH values, in plants, and consequently, in food [1].

Most of the Al(III) absorbed by humans comes from food and water [2]. The toxicity of this element to the human body and its strong distribution in the ecosystem, such as water and soil, is a constant concern for public health, which justifies the interest in developing simpler and faster methods for its determination.

There are several analytical methods for the determination of Al(III) in biological and environmental samples, such as inductively coupled plasma atomic emission spectrometry (ICP-AES), graphite furnace atomic absorption spectrometry (GF-AAS), visible spectrophotometry, fluorimetry, and voltammetry [3]. Some of these methods are not suitable for the analysis of real samples involving complex matrices. Thus, it is necessary to develop new methods that allow for increased sensitivity and selectivity of detection methods and that eliminate the sample treatment step, thus being less laborious [4].

Alternatively, electroanalytical techniques such as voltammetry offer important advantages compared to spectrometric techniques, such as high sensitivity, low detection limit, relative simplicity, and low equipment cost [5]. However, direct voltammetric determination of Al(III) is not possible due to its reduction potential being very negative and very close to the reduction potential of the hydrogen ion. However, Al(III) can be determined indirectly by differential pulse voltammetry in the presence of complexing agents [6], such as solochrome violet RS, sodium 1,2-dihydroxyanthraquinone-3-sulfonate (alizarin red S), cupferron [2].

Thus, the objective of this work was to determine Al(III) by differential pulse voltammetry (DPV) indirectly by complexation with alizarin red S. Experimental designs and response surface methodology were used in order to optimize the voltammetric response, to achieve lower concentration levels of this element aiming at an alternative method to the current ones.

## 2 MATERIALS AND METHODS

### 2.1 Equipment for voltammetric measurements

The Metrohm 797 VA Computrace voltammetric analyzer was used, with a hanging drop mercury electrode (HMDE) as the working electrode, an Ag/AgCl (3 mol $L^{-1}$ KCl) reference electrode, and a platinum wire as the auxiliary electrode. The potentiostat operates interfaced to a microcomputer via USB, and the system is managed by the 797 VA Computrace software, version 1.2. The data were processed using Origin Pro 9.1 [7] and Statistica 7.0 [8] programs.

#### 2.1.1 Reagents and Solutions

All solutions were prepared in deionized water. A 1000 mg $L^{-1}$ Al(III) stock solution was obtained by dissolving $Al_2(SO_4)_3$. Solutions with concentrations from 0.1 to 100 mg $L^{-1}$ were obtained by successive dilutions of the stock solution.

A 1 g $L^{-1}$ Ca(II) solution was prepared by diluting the salt $CaCl_2$, and by diluting the stock solution, a solution with a concentration of 1 mg $L^{-1}$ was obtained. A 0.005 mol $L^{-1}$ stock solution of alizarin red S (ARS) was prepared. A 0.1 mol $L^{-1}$ potassium bromate solution was prepared by dissolving $KBrO_3$. A 1 mol $L^{-1}$ ammonium chloride solution, with pH 9.2, used as a supporting electrolyte, was obtained by dissolving $NH_4Cl$.

### 2.2 Voltammetric procedure

Initially, the electrochemical behavior of the complex formed between Al(III) and alizarin red S was evaluated by cyclic voltammetry. For this, the first scan consisted of adding 1.00 mL of the supporting electrolyte ($NH_4Cl$) and 10.0 mL of deionized water to the voltammetric cell; the solution was purged under stirring by passing ultrapure nitrogen for 300 s, obtaining the voltammogram of the supporting electrolyte, which is the blank test.

In the second scan, the same procedure was performed, adding 1.00 mL of supporting electrolyte ($NH_4Cl$), 10.0 mL of deionized water, 100 µL of 1 mg $L^{-1}$ Ca(II), 1.00 mL of 0.1 mol $L^{-1}$ $KBrO_3$, and 100 µL of alizarin red S (0.005 mol $L^{-1}$), purged for 60 s, and the voltammogram was acquired, which is that of alizarin red S.

Finally, for a third scan, the same reagents from the second analysis were added to the voltammetric cell, along with 50 µL of 10 mg $L^{-1}$ Al(III) to obtain the voltammogram of the alizarin-Al(III) complex.

The voltammetric conditions employed in cyclic voltammetry were a forward potential sweep from 0.0 to -1.2 V, an equilibrium time of 5 s, a voltage step of 5 mV, and a sweep rate of 25 mV $s^{-1}$. Three sweeps were performed in each experiment, and the average of the maximum peak currents was recorded at the Al(III) determination potential.

The voltammetric conditions employed in differential pulse voltammetry were a potential range of -0.9 to -1.2 V and an equilibrium time of 5 s. The parameters evaluated were voltage step (3 to 10 mV), pulse amplitude (20 to 50 mV), pulse time (10 to 25 ms), and voltage step time (0.2 to 0.5 s). Only the Al(III) concentration was varied, with the addition of 50 µL at a concentration of 10 mg $L^{-1}$.

For sample analysis, the 10 mL of deionized water is replaced with the same volume of water from the treatment plants.

### 2.3 Experimental Design

In order to define which variables significantly affect the voltammetric response, a full $2^5$ factorial design was carried out. Five variables were evaluated, totaling 32 trials. The Statistica 7.0 [8] was used to generate the experimental design and perform the analysis of the results.

After analyzing the results of the full factorial design, a central composite design was carried out, with five central points, with the selected independent variables: pulse amplitude (PA) and pulse time (PT).

### 2.4 Samples

Water samples were collected at the UFV Water Treatment Plant (WTP) and at the Water Treatment Plant of the Autonomous Water and Sewage Service of Viçosa (SAAE) at three different points of the plants; Raw water was collected from the source (Sample 1), the second sample was collected during the flocculation stage, after the addition of Al(III) sulfate (Sample 2), and the third was collected from the treated water reservoir, ready for consumption (Sample 3).

For the determination of sample 1, from both treatment plants, it was necessary to carry out treatment with nitric acid and hydrogen peroxide, since organic matter is a possible interferent.

Samples 2 did not require specific treatment. In sample 3, from both the WTP and the SAAE, Al(III) was not detected, so the samples were fortified with Al(III) for later determination. Thus, instead of adding 10 mL of water, the samples were added in the same volume.

## 3 RESULTS AND DISCUSSION

### 3.1 Voltammetric Behavior of Al(III) in the Presence of Alizarin Red S (ARS)

Cyclic voltammograms, in the potential range of 0 to -1.2 V, with a scan rate of 25 mV $s^{-1}$ are shown in figure 1(A). These voltammograms illustrate the voltammetric behavior of alizarin red S in the presence and absence of Al(III).

It is noted that during the cathodic scan, the ligand reduction signal in the absence of Al(III) occurs at -0.65 V, and a peak corresponding to its oxidation showed a slight shift, appearing at -0.62 V. A second irreversible peak appears at -1.02 V, as already observed by Van den Berg et al. [9].

After the addition of Al(III), an irreversible reduction peak of alizarin red S was observed at a potential of -1.07 V, due to the adsorption of the ARS-Al complex on the electrode. These results suggest that there is an interaction between Al(III) and the alizarin S red ligand. The addition of $Ca^{2+}$ and $KBrO_3$ was carried out to minimize possible interference from the signal related to the complex. With these additions, a shift of the second reduction peak of alizarin S red to more anodic potentials is observed, thus allowing a better separation of the peaks of the ARS-Al complex and ARS. This shift is due to the formation of a calcium ion complex with ARS a potential of -0.88 V, in which $Ca^{2+}$ forms a complex with the excess alizarin S red, causing it to be shifted to more anodic potentials, thus reducing interference in the ARS-Al signal.

Figure 1(B) shows the enlargement of the region of interest of the study in which the emergence of a discrete peak related to the ARS-Al complex is observed.

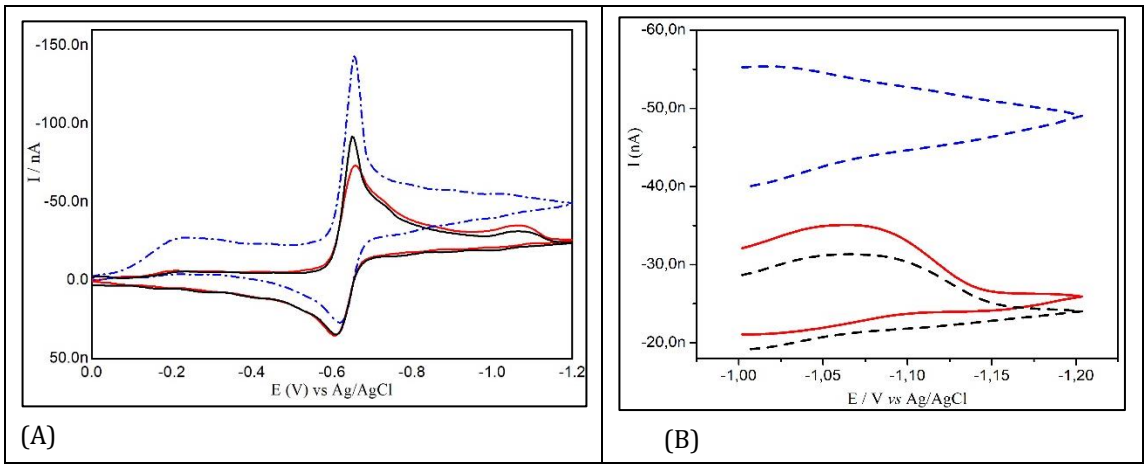



**Figure 1: A) Cyclic voltammograms of the voltammetric behavior of ARS in the absence and presence of Al(III), at pH 9.20 and a scan rate of 25 mV $s^{-1}$. B) Enlarged region of interest:**

ARS solution in $NH_4Cl$ medium, pH 9.20 in blue dashed line. ARS solution in $Ca^{2+}$ and $KBrO_3$ medium in black dashed line. ARS solution in $Ca^{2+}$, $KBrO_3$ and Al(III) medium in red line.

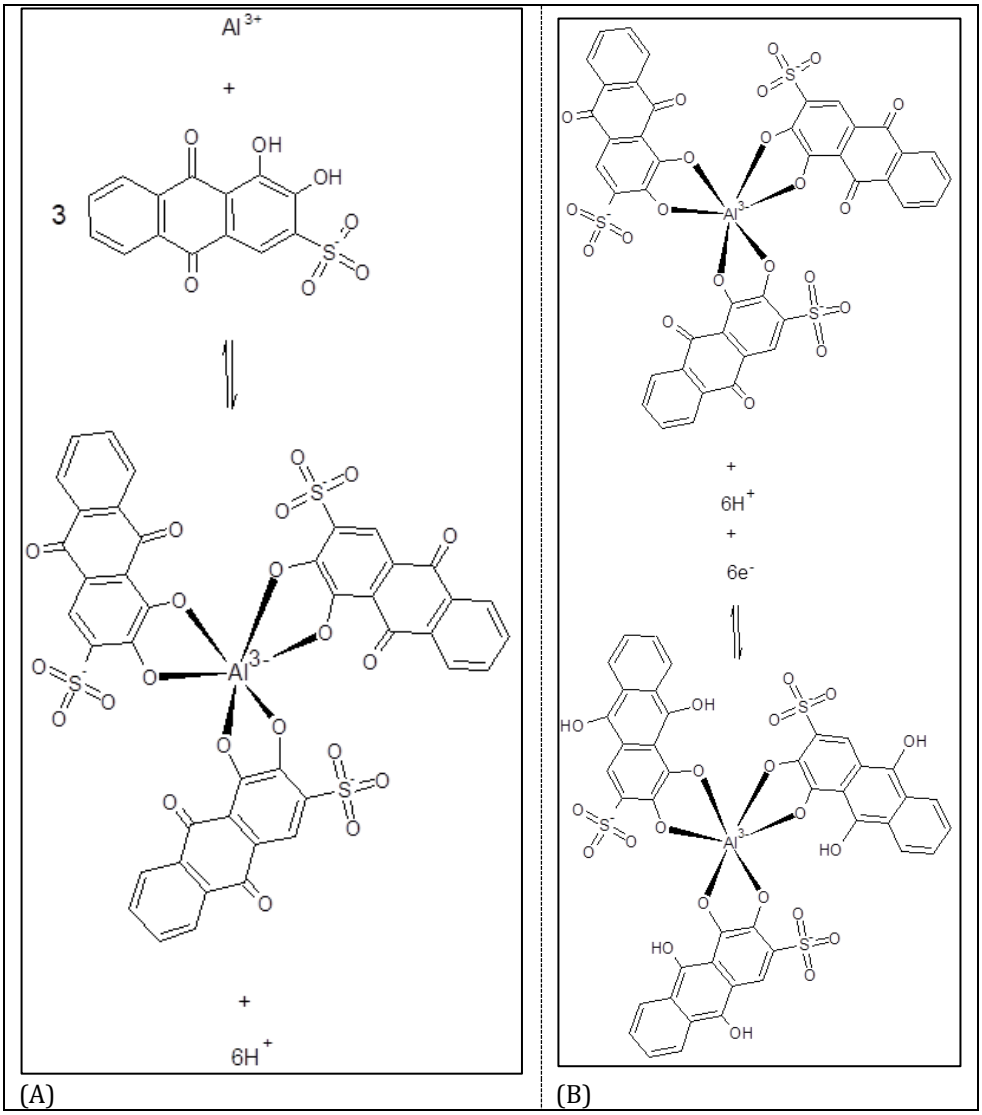



**Figure 2: (A) Proposed complexation reaction of ARS with Al(III).; (B) Proposed reduction reaction of the ARS-Al complex.**

A proposed explanation for the complexation reaction of ARS with Al can be found in figure 2(A). In the absence of Al(III), the reduction of the free ligand is due to the reduction of the anthraquinonyl group to dihydroanthraquinonyl. Thus, the reduction reaction of the ARS-Al complex can be shown in figure 2(B).

### 3.2 Study of voltammetric parameters for optimizing the voltammetric response

Preliminary studies were carried out with the voltammetric parameters for the differential pulse sweep, respecting the quantities of each reagent as per item 2.3.

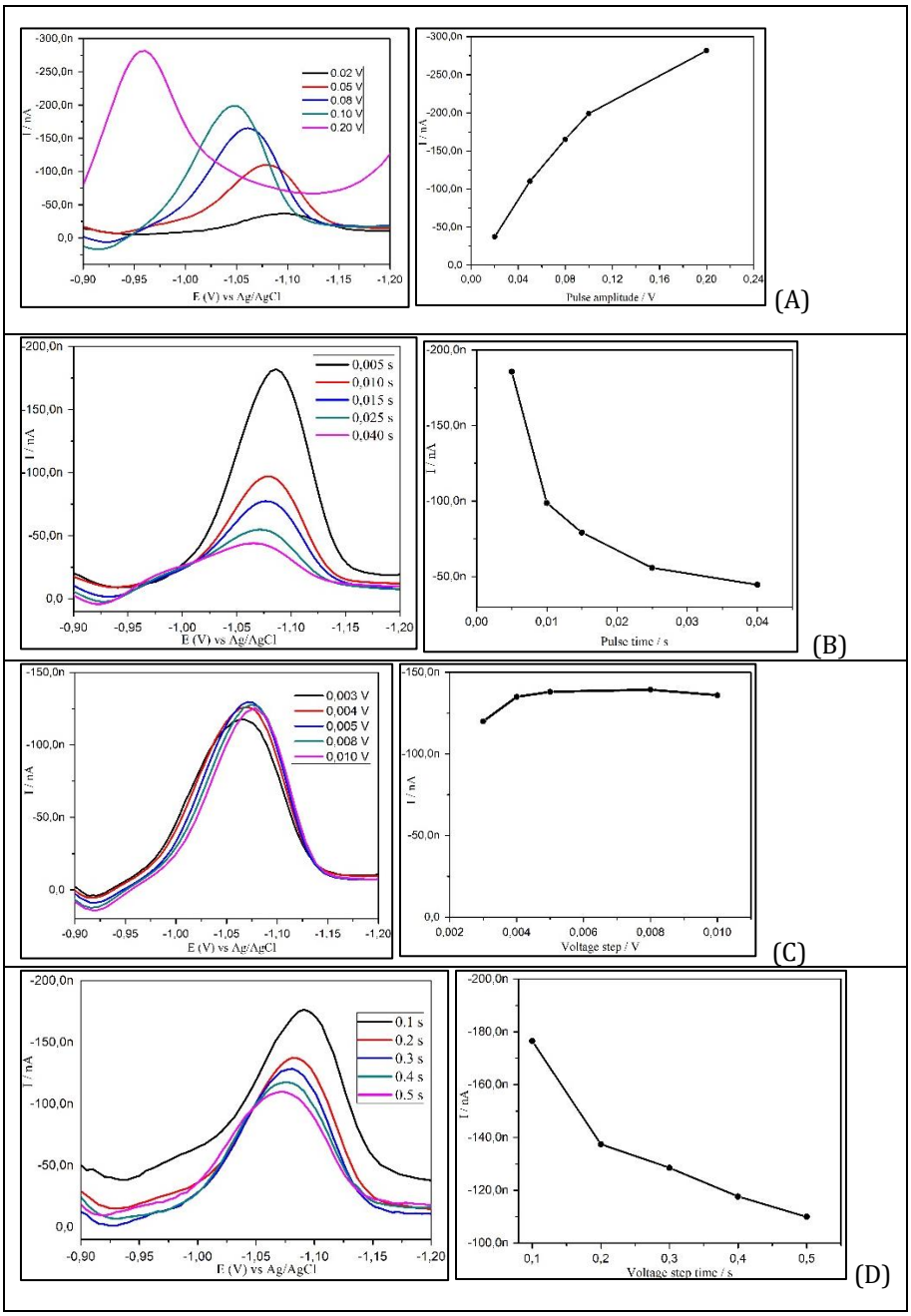



**Figure 3: Study of the parameters Pulse Amplitude (A), Pulse Time (B), Voltage Step (C) and Voltage Step Time (D).**

The parameters chosen were pulse amplitude (PA), pulse time (PT), voltage step (VS), pulse time (PT) and voltage step time (VST). The study was conducted by fixing pre-established values for the unobserved factors and varying the values for the factor under study. The droplet area was fixed at 0.7 $mm^2$, according to the device instructions.

Figure 3(A) shows the variation in pulse amplitude (PA), observing that the amplitude proved to be responsible up to a certain value for the increase in current. However, for values above 0.1 volt there was a shift in the half-wave potential to more positive values, moving away from the region of interest. Thus, the levels chosen for the pulse amplitude were 0.02 V and 0.05 V.

In figure 3(B) the variation in pulse time (PT) was analyzed, which also proved to be inverse to the increase in current, which also highlights the importance of a fast sweep. Thus, the values chosen for this factor were 0.015 and 0.025 s.

The variation in the voltage step (VS) value, as shown in the graph in figure 3(C), practically did not contribute to the increase in the voltammetric response, therefore the value 0.005 V was fixed for this parameter for subsequent studies.

The voltage step time (VST) proved to be inversely proportional to the increase in current, which highlights the importance of a fast sweep. For this parameter (Figure 3(D)), the peak shifts to values above 0.1 and to values below 0.5 it showed very low current values. Therefore, the values chosen for this factor were 0.2 s and 0.5 s.

### 3.3 Factorial Design – Factor Screening

Based on preliminary experiments, a full $2^5$ factorial design was executed with the main objective of screening the factors that influence the voltammetric response in the differential pulse scan. According to the study done previously, adding the pretreatment factors, such as deposition potential (DP) and deposition time (DT), these were chosen with their respective levels (Table 1).

Adopting the random order of the experiments, the experimental design matrix was obtained with the coded values of the independent variables. The voltammetric responses were obtained from the current peaks of the ARS–Al complex. The data relating to the responses were processed to obtain the effects of the variables (Table 2).

**Table 1: Factors and levels chosen for the full factorial design $2^5$.**

| Symbol | Factors | Level - | Level + |
|---|---|---|---|
| PA | Pulse Amplitude (V) | 0.200 | 0.050 |
| PT | Pulse Time (s) | 0.015 | 0.025 |
| VST | Voltage Step Time (s) | 0.200 | 0.500 |
| DP | Deposition Voltage (V) | -0.800 | -1.100 |
| DT | Deposition Time (s) | 0.000 | 30.000 |

**Table 2: Full factorial design $2^5$ and respective responses for DPV.**

| Experiment | Factors | | | | | Response µA |
|---|---|---|---|---|---|---|
| | PA | PT | VST | DP | DT | |
| 1 | -1 | -1 | -1 | -1 | -1 | -43.82 |
| 2 | 1 | -1 | -1 | -1 | -1 | -173.07 |
| 3 | -1 | 1 | -1 | -1 | -1 | -23.90 |
| 4 | 1 | 1 | -1 | -1 | -1 | -66.08 |
| 5 | -1 | -1 | 1 | -1 | -1 | -40.89 |
| 6 | 1 | -1 | 1 | -1 | -1 | -160.45 |
| 7 | -1 | 1 | 1 | -1 | -1 | -18.14 |
| 8 | 1 | 1 | 1 | -1 | -1 | -70.29 |
| 9 | -1 | -1 | -1 | 1 | -1 | -47.58 |
| 10 | 1 | -1 | -1 | 1 | -1 | -194.80 |
| 11 | -1 | 1 | -1 | 1 | -1 | -24.10 |
| 12 | 1 | 1 | -1 | 1 | -1 | -69.15 |
| 13 | -1 | -1 | 1 | 1 | -1 | -34.81 |
| 14 | 1 | -1 | 1 | 1 | -1 | -144.16 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 15 | -1 | 1 | 1 | 1 | -1 | -18.55 |
| 16 | 1 | 1 | 1 | 1 | -1 | -56.09 |
| 17 | -1 | -1 | -1 | -1 | 1 | -57.47 |
| 18 | 1 | -1 | -1 | -1 | 1 | -204.12 |
| 19 | -1 | 1 | -1 | -1 | 1 | -28.60 |
| 20 | 1 | 1 | -1 | -1 | 1 | -77.00 |
| 21 | -1 | -1 | 1 | -1 | 1 | -36.00 |
| 22 | 1 | -1 | 1 | -1 | 1 | -167.56 |
| 23 | -1 | 1 | 1 | -1 | 1 | -18.00 |
| 24 | 1 | 1 | 1 | -1 | 1 | -64.07 |
| 25 | -1 | -1 | -1 | 1 | 1 | -51.45 |
| 26 | 1 | -1 | -1 | 1 | 1 | -88.75 |
| 27 | -1 | 1 | -1 | 1 | 1 | -24.30 |
| 28 | 1 | 1 | -1 | 1 | 1 | -74.83 |
| 29 | -1 | -1 | 1 | 1 | 1 | -37.28 |
| 30 | 1 | -1 | 1 | 1 | 1 | -154.15 |
| 31 | -1 | 1 | 1 | 1 | 1 | -16.62 |
| 32 | 1 | 1 | 1 | 1 | 1 | -68.74 |

According to the results shown in table 3, the main effects pulse amplitude (PA) and pulse time (PT) were the only significant main effects, as well as the second-order interaction of these effects. From this design, it was possible to construct the Pareto chart (Figure 4), which allowed for the statistical analysis estimation of the effects of the variables on the voltammetric response, at a 95% confidence level. The pulse amplitude (PA) variable exerts a negative effect on the current intensity of the complex, and the pulse time (PT) exerts a positive effect. Thus, it can be understood that the best current response values are obtained at the high level for PA (+) and at the low level for PT (–), due to the negative current values.

**Table 3: Effects and errors for the full factorial design $2^5$.**

| **Effects estimates ± Standard error** | | **Relation t(16)** |
|---|---|---|
| Média | -73.79 ± 3.54 | 20.84 |
| Main effects | | |
| PA | -82.40 ± 7.08 | 11.54 |
| PT | 57.70 ± 7.08 | 8.15 |
| VST | 8.54 ± 7.08 | 1.21 |
| DP | 9.34 ±7.08 | 1.32 |
| DT | 1.47 ± 7.08 | 0.21 |
| Effcts of 2ª order interaction | | |
| PA x PT | 35.67 ±7.08 | 5.02 |
| PA x VST | -1.58 ± 7.08 | 0.22 |
| PA x DP | 7.83 ± 7.08 | 1.11 |
| PA x DT | 3.71 ± 7.08 | 0.52 |
| PT x VST | -1.43 ± 7.08 | 0.20 |

| | | |
|---|---|---|
| PT x DP | -7.71 ± 7.08 | 1.09 |
| PT x DT | -4.63 ± 7.08 | 0.65 |
| VST x DT | -3.04 ± 7.08 | 0.43 |
| VST x DT | -3.03 ± 7.08 | 0.43 |
| DP x DT | 7.74 ±7.08 | 1.09 |

The highlighted effects were significant according to the t-test. (α = 0.05).

The voltage step time variable was not significant, being fixed at the lowest level (-) at 0.2 s, ensuring a greater number of points in the voltammogram and, consequently, better resolution. It can be verified that the variables, deposition potential and deposition time, do not interfere with the current intensity. Therefore, any of the levels studied could be chosen, and in this case, the levels were fixed at -800 mV and 0 s, respectively.

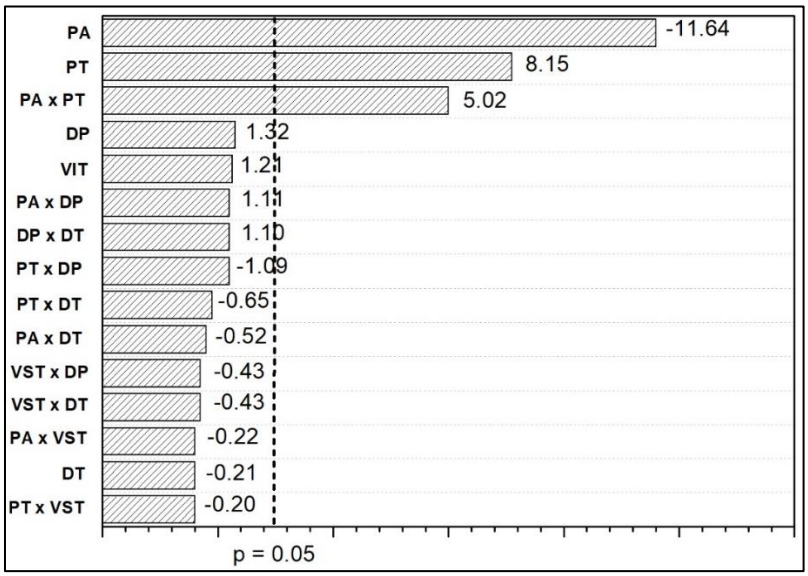



**Figure 4: Pareto chart with the estimated effects (absolute values)of the variables tested in the full factorial design $2^5$.**

### 3.4 Response Surface Methodology

After screening the factors using a full factorial design 25, the Response Surface Methodology was implemented employing a central composite design (CCD) for the selected independent variables, pulse amplitude (PA) and pulse time (PT). For the PA factor, the chosen level -1 was a value greater than the factorial design value, equal to 0.03 volts, and the +1 level was equal to the highest level of the factorial design. For the PT factor, the -1 and +1 levels were the same as those used in the factorial design. The remaining levels are presented in table 4.

**Table 4: Factors and levels chosen for CCD design for DPV.**

| **Variables** | **Levels** | | | | |
|---|---|---|---|---|---|
| | -1.414 | -1 | 0 | 1 | 1.414 |
| Pulse amplitude (mV) | 25.858 | 30 | 40 | 50 | 54.142 |
| Pulse time (ms) | 12.929 | 15 | 29 | 25 | 27.071 |

The central composite design (with α = 1.414) for the two factors under the described conditions is presented in Table 5, with the values of the coded levels and the responses obtained by the peak current height of the ARS–Al complex, with five repetitions at the central point.

**Table 5: Central composite design matrix with coded values and voltammetric signal responses of the ARS-Al complex, with k = 2 and α = 1.414 for the DPV.**

| Experiment | Levels factors | | Response (nA) |
|---|---|---|---|
| | PA | PT | |
| 1 | -1 | -1 | -53.05 |
| 2 | 1 | -1 | -99.49 |
| 3 | -1 | 1 | -34.85 |
| 4 | 1 | 1 | -62.42 |
| 5 | -1.414 | 0 | -40.31 |
| 6 | 1.414 | 0 | -99.20 |
| 7 | 0 | -1.414 | -93.78 |
| 8 | 0 | -1.414 | -44.54 |
| 9 | 0 | 0 | -64.28 |
| 10 | 0 | 0 | -53.61 |
| 11 | 0 | 0 | -59.00 |
| 12 | 0 | 0 | -58.71 |
| 13 | 0 | 0 | -71.51 |

Table 6 presents the regression model coefficients, errors, and confidence limits for the voltammetric response at the 95% confidence level, which were obtained using Microsoft® Excel spreadsheets [10].

t can be observed that for the highlighted independent variables, the linear term pulse amplitude and pulse time significantly influenced the voltammetric response.

**Table 6: Coefficients and pure error for the response surface model.**

| Coeficients ± Error | | t | p |
|---|---|---|---|
| Average | -64.212 ± 1.808 | 35.516 | 5.5E-11 |
| PA | -19.662 ± 2.305 | 8.531 | 1.3E-05 |
| PT | 15.613 ± 2.305 | 6.774 | 8.1E-05 |
| PA x PT | 4.718 ± 3.259 | 1.447 | 0.18172 |

* $t_{tab}$ (9) = 2.26, $\alpha$ = 0.05

Equation 4 presents the model fitted for the significant coefficients and their respective errors, as a function of pulse amplitude and pulse time.

$$z = -64.212 - 19.662 \cdot PA + 15.613 \cdot PT \quad (4)$$
$$\pm 1.808 \quad \pm 2.305 \quad \pm 2.305$$

Figure 5 shows the contour lines of the model, and through them the maximum response obtained can be verified.

The pulse amplitude factor, when used at the highest level of the values encoded on the response surface, contributes to the greatest voltammetric response; that is, values close to 50 mV show the highest current value in magnitude. As mentioned earlier, since it is a cathode sweep, the maximum response is the most negative value. Analyzing the surfaces, one might assume that further increasing the amplitude value would increase the voltammetric response; however, as already mentioned, values above 50 mV would shift the half-wave potential to more positive values, moving away from the region of interest.

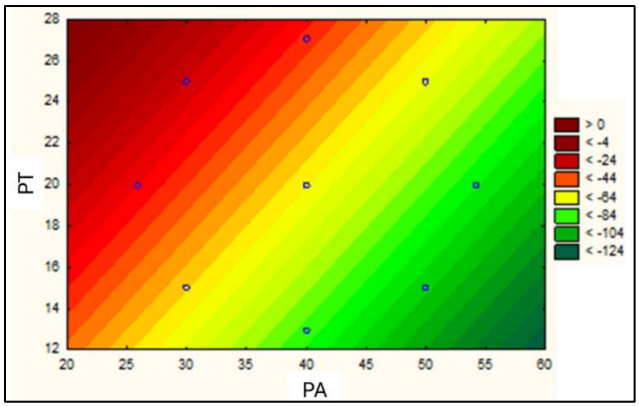


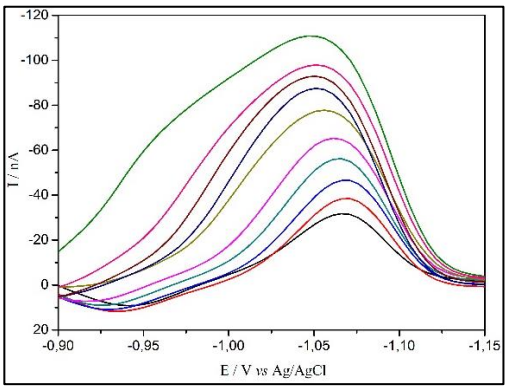

**Figure 5: Level curves of the current response of the ARS–Al complex.**

For the pulse time factor, the best results were found at its lowest level. Therefore, values close to 15 ms contribute to a greater voltammetric response. Thus, 50 mV was chosen for the pulse amplitude and 15 ms for the pulse time.

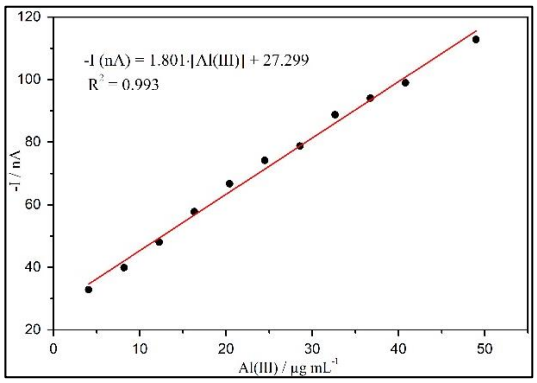
Thus, after optimizing the parameters, the optimal values and the estimated and observed responses for the ARS-Al complex and the relative error are shown in table 7.

**Table 7: Optimized parameters for Al(III) analysis by differential pulse voltammetry.**

| **Parameters** | **Optimal values** | **Estimated current** |
|---|---|---|
| Initial potential | -0.9 V | -103.60 nA |
| Final potential | -1.2 V | |
| Pulse amplitude | 50 mV | |
| Pulse time | 15 ms | |
| Voltage step timeVoltage incremetiremento de voltagem | 5 mV | Observed current observada |
| Voltage step time | 0.2 s | -99.49 nA |
| Scan speed | 25 $mVs^{-1}$ | |
| Equilibrium time equilíbrio | 5 s | |
| Drop size (área) | 0.70 $mm^2$ | Relative error: 3.97 % |




(A)




(B)

**Figure 6: Optimized parameters for Al(III) analysis by differential pulse voltammetry.**

The method's ability to provide results directly proportional to the analyte concentration within an application range [11] was established for the determination of Al(III) in the presence of the ARS complexing agent, based on the proposed

methodology. The range was established between 4.00 μg $mL^{-1}$ and 50.00 μg $mL^{-1}$. The results are shown in figures 6(A) and 6(B).

The standard deviation of the blank for the voltammetric methodology for Al(III) determination was calculated using ten repetitions of the blank (ARS and supporting electrolyte) performed on the same day, under the same analytical conditions for samples without any Al(III) residue. The limits of detection and quantification were calculated, obtaining LOD = 0.25 μg $mL^{-1}$ and LOQ = 0.82 μg $mL^{-1}$.

With the results obtained, it is verified that after the use of experimentals designs, the proposed methodology presented limits of detection and quantification lower than those described in the literature when employing the same technique [5].

The repeatability of the independent voltammetric responses was evaluated using eight replicates of an Al(III) standard solution. The analyses were performed on the same day and under the same conditions, obtaining a relative standard deviation (RSD) of 2.37%. This result shows good repeatability and a low deviation between determinations.

### 3.5 Study of Interfering Substances for Al(III) Analysis in Water

Some metallic ions can interfere with the voltammetric determination of Al(III) using Alizarin Red S. These species can produce current peaks close to the peak of the ARS-Al complex. Therefore, interference studies were conducted on the developed procedure to evaluate the limits of application for determinations in real water samples.

Among the metallic ions that can interfere with the voltammetric determination of Al using ARS, the influence of Cu, Fe, Mn, and Zn, which may be present in water, were systematically investigated under the optimized conditions described for the method (Table 8). The additions of these ions were in concentrations up to 200 times greater than that of Al(III) in the voltammetric cell.

From table 8, it can be inferred that for Al(III) at a concentration of 5 μg $L^{-1}$, the interfering substances Cu(II) up to 4 mg $L^{-1}$, Fe(III) up to 40 mg $L^{-1}$, Mn(II) up to 4 mg $L^{-1}$ and Zn(II) up to 0.2 mg $L^{-1}$ did not affect the initial current

**Table 8: Study of possible interfering substances Cu, Fe, Mn and Zn for the analysis of Al in water, for an Al(III) concentration of 20 μg $L^{-1}$, in the voltammetric cell.**

| **Cu(II)** | **mg $L^{-1}$** | **0** | **0.02** | **0.2** | **2** | **4** |
|---|---|---|---|---|---|---|
| | I (nA) | -34.17 | -35.68 | -33.85 | -36.38 | -32.81 |
| Fe(III) | mg $L^{-1}$ | 0 | 10 | 30 | 40 | 100 |
| | I (nA) | -34.20 | -34.36 | -35.14 | -34.63 | -21.65 |
| Mn(II) | mg $L^{-1}$ | 0 | 0.02 | 0.2 | 2 | 4 |
| | I (nA) | -33.90 | -34.98 | -34.00 | -33.19 | -34.29 |
| Zn(II) | mg $L^{-1}$ | 0 | 0.02 | 0.2 | 0.4 | 0.8 |
| | I (nA) | -34.30 | -33.06 | -52.86 | -70.36 | -85.79 |

### 3.6 Applicability of the optimized technique to water samples

The validated method was applied to detect Al(III) in water samples at the UFV Water Treatment Plant (ETA) and the Viçosa Autonomous Water and Sewage Service (SAAE), both located in the city of Viçosa, Minas Gerais, Brazil.

For the determination of Al(III), 10 mL of deionized water, 1 mL of ammonium chloride buffer solution, 1 mL of $KBrO_3$, and 100 μL of $Ca^{2+}$ were transferred to the voltammetric cell. These were deoxygenated by bubbling ultrapure nitrogen gas for 5 minutes, and the reading was recorded as blank. Then, a 100 μL aliquot of ARS complexing agent was added, deoxygenated for one minute, and the reading was recorded. Finally, 50 μL of the water sample was added, deoxygenated for another minute, thus recording the voltammogram of the sample. All readings were taken in triplicate, and the averages of the voltammograms were recorded; figure 7 exemplifies the case of sample 1 from the WTP.

In all three locations at each station, Al(III) was found in samples 1 and 2, for both the WTP and the SAAE. In sample 3 for both treatment plants, no Al(III) was detected. The results for all samples are shown in table 10, with all analyses

performed in triplicate. From the analytical curve (Figure 6B), it was possible to find the concentration values of the samples.

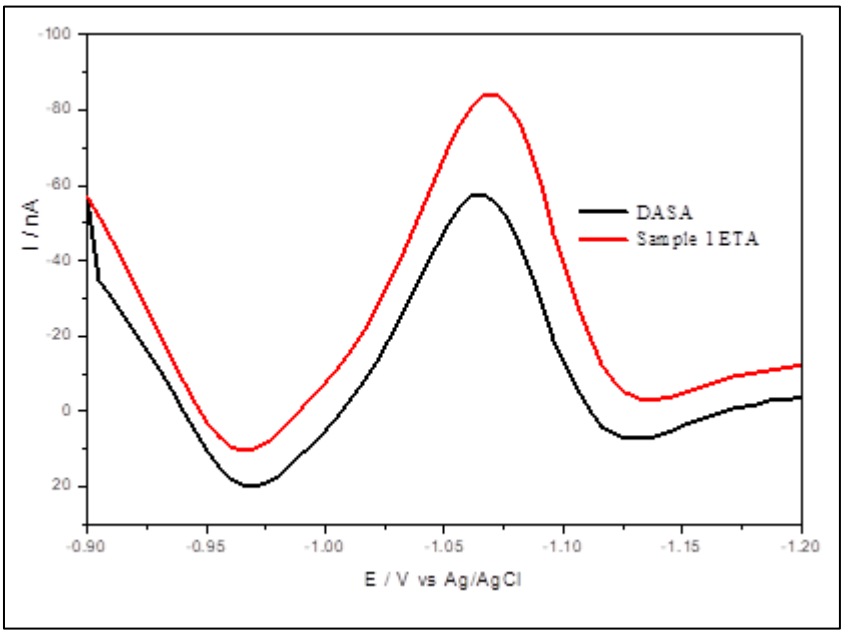



**Figure 7: Example of voltammograms obtained from sample 1 of the ETA.**

To compare the proposed method, the samples were determined by Atomic Absorption Spectrophotometry (AAS), and the results are presented in table 9.

**Table 9: Results of determinations performed by AAS and by the voltammetric method for Al(III) in the samples.**

| **Samples** | **Al(III) Concentration (mg $L^{-1}$)** | |
|---|---|---|
| | Atual method | EAA |
| ETA | | |
| 1 | 0.116 ± 0.008 | 0.118 ± 0.007 |
| 2 | 0.149 ± 0.013 | 0.150 ± 0.006 |
| 3 | ND* | ND* |
| SAAE | | |
| 1 | 0.248 ± 0.014 | 0.254 ± 0.020 |
| 2 | 0.155 ± 0.005 | 0.160 ± 0.015 |
| 3 | ND* | ND* |

* ND – Not detected.

It can be observed that the two methods present similar values for all samples. The results showed that the proposed method is accurate, and it does not require any separation or pre-concentration of the samples.

According to these results, the Al(III) levels in the samples from point 3 (water ready for consumption) from both treatment plants are below the detection limit, as established by the WHO and defined by Ordinance 2.914 of the Brazilian Ministry of Health, therefore, they do not pose a risk of being consumed.

## 4 CONCLUSION

The proposed method for the detection and determination of Al(III) by complexation with ARS, using the differential pulse voltammetry technique with a hanging drop mercury electrode, proved to be a very attractive, simple, precise, and reproducible tool, suitable for the determination of Al(III) at trace concentrations.

The factorial design enabled the optimization of the voltammetric technique, and the optimization procedures were effective; and based on the voltammetric parameters achieved using the differential pulse voltammetry technique, the detection limits were determined, and the methodology was validated.

The voltammetric method was validated by comparing the results obtained with a reference method, atomic absorption spectroscopy, which showed statistically similar results.

## STATEMENTS ON COMPLIANCE WITH ETHICAL STANDARDS

### *Acknowledgments*

The authors thank CAPES for the master's degree grant to the first author (C.O.M.).

### *Funding Source*

This work was financially supported by FAPEMIG and CAPES.

### *Disclosure of conflict of interest*

The authors declare that no known conflict of interest or personal relationships have influenced the work reported in this paper.

### *Statement of informed consent*

Informed consent was obtained from all individual participants included in the study.

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