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PII: S0039-9140(18)31312-2
DOI: <https://doi.org/10.1016/j.talanta.2018.12.048>
Reference: TAL19396

To appear in: *Talanta*

Received date: 6 November 2018
Revised date: 12 December 2018
Accepted date: 14 December 2018

Cite this article as: Olga Domínguez-Renedo, A. Marta Navarro-Cuñado, Eduardo Ventas-Romay and M. Asunción Alonso-Lomillo, Determination of Aluminium using different techniques based on the Al(III)-morin complex, *Talanta*, <https://doi.org/10.1016/j.talanta.2018.12.048>

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**DETERMINATION OF ALUMINIUM USING DIFFERENT TECHNIQUES
BASED ON THE Al(III)-MORIN COMPLEX**

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Abstract

Three different methods for the determination of Al(III) in aqueous samples were compared. The different described procedures were based on the formation of the Al(III)-morin complex. UV-Vis spectrophotometry, spectrofluorimetry and differential pulse adsorptive stripping voltammetry (DPAdSV) techniques were compared under optimized experimental conditions. The DPAdSV method showed a better performance for the analysis of Al(III) in terms of capability of detection (70 nM) in comparison with the value obtained for UV-Vis spectrophotometric (300 nM) and spectrofluorimetric (110 nM) techniques. Thus, DPAdSV method was selected for the analysis of aluminium in river, tap and bottled water samples under the following optimized experimental conditions: pH = 4.4, deposition potential = +243 mV, deposition time = 210 s, giving satisfactory results.

Keywords: Aluminium; Morin; Stripping voltammetry; UV–Vis spectroscopy; Fluorescence; Water samples

1. Introduction

Aluminium is a widely dispersed element on earth being the third most abundant component of the earth's crust (approximately 8 %) [1, 2]. It has been reported as an important toxic metal towards fish, algae and plant roots in acidic media [3]. Moreover, it has been related with an important number of human disorders including Alzheimer's disease, Parkinson's dementia, amyotrophic lateral sclerosis, and other diseases like osteodystrophy and noniron deficiency microcytic anemia [4, 5].

Human exposure to aluminium has nowadays intensely increased mainly due to acid rains, which cause partial dissolution of soil aluminium, leading to a growth in its concentration in natural waters and biological systems [6]. High aluminium levels may also be present in tap and drinking waters since commercial aluminium salts are often used as flocculants in water treatment plants [7]. Moreover, the many industrial applications of this metal, namely fabrication of automobiles, packaging materials, electrical equipment and production of metal alloys and building construction materials, get humans in direct contact with this toxic metal [8].

Many sensitive, simple and reliable analytical methods for the determination of aluminium in different matrices have then been reported. Aluminium determination is commonly performed using classical spectroscopic techniques, such as atomic absorption or emission spectrophotometry. However, these methods are time and money consuming and do not allow real-time or even on-site determinations due to their bulky instrumentation and tedious sample preparation processes [9-11]. The determination of

aluminium based on the formation of UV-Vis absorptive complexes represents a simpler system for the analysis of this metal (Table 1). In this way, pyrocatechol violet [12], morin [13, 14] and alizarin red S [15] have often been selected as complexing agents for the analysis of aluminium, although these methods present poor sensitivity. Moreover, the determination of aluminium has been performed by other spectrophotometric methods based on the formation of fluorescent complexes with different reagents including 5,7-dibromo-8-quinolinol [16], salicylaldehyde picolinoylhydrazone [17], 8-hydroxyquinoline [6], 8-hydroxyquinoline-5-sulfonic acid [9], lumogallion [18-20] and morin [21, 22]. These works are characterized by a high level of sensitivity, achieving limits of detection of nM order (Table 1).

The analysis of aluminium has also been performed by means of electroanalytical techniques. These techniques present significant advantages including speed, high selectivity and sensitivity, simplicity and low equipment cost [4]. The voltammetric determination of aluminium is difficult due to its particular electrochemical behaviour, since it is reduced at such high potential (-1.75V versus SCE) that is associated with problems from the hydrogen background current [5]. Therefore, the usual electrochemical determination of this metal has been carried out in the presence of a complexing agent. Due to the adsorption of the aluminium complex on the working electrode surface, the reduction potential displaces to more positive values [4, 5]. Most of the works based on this procedure use a hanging drop mercury electrode (HDME) as working electrode [23-39]. Spite of the high sensitivity of this electrode in the determination of metal species, it has to be considered the mercury toxicity. The unfriendly environmental effects of HDME can be reduced by using other kind of electrodes, including screen-printed electrodes [40] and glassy carbon electrodes (GCE) [41-45]. These devices are also based on the formation of a complex between

aluminium and ligands namely, alizarin red S [41], alizarin [40, 42], 8-hydroxyquinoline [43] and cupferron [44, 45], being often characterized by tedious and time consuming modification procedures of the working electrode. This work describes a new approach for the environmental friendly analysis of aluminium using morin and a GCE, by means of differential pulse adsorptive stripping voltammetry (DPVAdSV). Good results have been described for this ligand in the analysis of metals such as cadmium [46, 47], lead [47, 48], copper and zinc [48]. To the best of the author's knowledge, morin has not been used as a complexing agent in the electrochemical determination of aluminium, although it has led to good results when using spectrophotometric techniques [13, 14, 21, 22]. In order to improve the results described in these previous works for the UV-Vis spectrophotometric and spectrofluorimetric analysis of aluminium, an optimization of the experimental conditions has also been performed.

2. Experimental

2.1. Reagents

All reagents used were of analytical-reagent grade. Ultrapure water obtained from a Milli-Q water purifier (Millipore, Bedford, MA, USA) was used for the preparation of all solutions. Acetic-acetate solutions were used in spectrophotometric and fluorescence analysis and as supporting electrolyte in electrochemical measurements. Acetic acid and sodium acetate trihydrate used were purchased from VWR chemicals.

Stock standard solutions of Al(III) were prepared by dissolving the adequate amount of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Probus, Spain) in acetic-acetate buffer solution. Morin stock

solutions were prepared by dissolving the appropriate quantity of the reagent (Ferosa, Sharlau, Spain) in ethanol (Panreac, Spain).

2.2. Apparatus

Absorption spectra were recorded on a Varian Cary 50 UV-Vis Spectrophotometer. Fluorescence spectra were obtained from a RF 5301 PC spectrofluorometer (Shimadzu) with a spectral slit width of 10 nm and 5 nm. Electrochemical measurements were performed on a CHI 1030 electrochemical workstation (CH Instruments, Texas, USA). The three electrode set-up consisted of a GCE, a platinum electrode, and a Ag/AgCl electrode as working, counter, and reference electrodes, respectively.

2.3. Software

STATGRAPHICS Centurion XVI was used for experimental design, data analysis and robust regressions [49]. DETARCHI was used for the estimation of the capability of detection with a given probability of false positive and negative [50].

2.4. UV-Vis measurements

Solutions containing different concentrations of Al(III) were prepared by adding a volume of 5 mL of a 400 μ M morin standard solution to a 25 mL volumetric flask, an aliquot of a 10 μ M Al(III) standard solution and acetic-acetate buffer solution (pH 4.5) to complete the volume, except for the optimization process.

The spectra of the solutions were recorded in the wavelength range from 200 nm up to 800 nm. The UV-Vis spectrophotometric detection was yielded by measuring the absorbance of the Al(III)-morin complex at 410 nm.

2.5. Fluorescence measurements

Solutions containing different concentrations of Al(III) were prepared by adding a volume of 400 μL of a 250 μM morin standard solution to a 10 mL volumetric flask, followed by the addition of an aliquot of a 5 μM standard Al(III) solution. The volume was finally completed with an acetic-acetate buffer solution (pH 5.0), except for the optimization process.

The emission spectra of the solutions were recorded in the wavelength range from 400 nm up to 650 nm, using 350 nm as the excitation wavelength. The spectrofluorimetric detection was achieved by measuring the fluorescence of the Al(III)-morin complex at 505 nm.

2.6. Electrochemical measurements

Differential pulse voltammetry (DPV) and DPVAdSV measurements were performed at room temperature (approx. 20 $^{\circ}\text{C}$) in a cell containing 15 mL of the supporting electrolyte solution (acetic-acetate buffer) of the desired pH. An aliquot of 10 μM aluminium and 10 mM morin solutions were added and the corresponding voltammogram was then recorded.

DPVAdSV were carried out under stirring conditions according to a suitable time and potential of accumulation for each experiment. When the deposition time had elapsed, the stirring was switched off and the solution was left to settle for an equilibrium time of 10 s.

DPV and DPVAdSV scans were performed from + 0.2 V to + 1.0 V with the amplitude, pulse width, sampling width and pulse period as 50 mV, 50 mV, 0.0167 s and 0.2 s, respectively.

The surface of the GCE was polished after each run by using an abrasive paper covered with alumina. The GCE was finally washed with deionized water after polishing.

The electrochemical detection was achieved by measuring the anodic current due to the oxidation of the Al(III)-morin complex at a potential of + 0.6 V aprox.

3. Results

3.1. UV-Vis measurements of Al(III)-morin complex

Fig 1. shows the absorption spectra obtained for morin and Al(III)-morin complex. A maximum absorption at a wavelength of about 350 nm was observed for morin in acetic-acetate medium, while the maximum absorption of the Al(III)-morin complex appeared at around 410 nm.

The concentration of morin and the pH of the buffer solution have a significant effect on the formation of the described complex, being therefore critical factors for the sensitive determination of Al(III). Thus, these variables were optimized in order to find the best possible analytical conditions. Experimental design was used as a tool to perform this optimization process, since it lets exploring a wide experimental range with a reduced number of experiments. Moreover, this methodology is more efficient than the “one-at-time” optimization process since it allows identifying possible interactions between factors that could lead to false conclusions [51]. A 2^2 central composite design was then performed, which implies 11 experiments corresponding to all the possible

combinations among the levels of the above-mentioned experimental variables, bearing in mind the three replications at the central point necessary to estimate the residual value. The optimum values found for these variables were 80 μM and 4.5 for the concentration of morin and pH, respectively.

Once the optimum parameters for the analysis were chosen, a calibration curve was constructed in order to estimate the linear range of the developed method. In this way, a linear relationship between absorbance value (A) at 410 nm and the concentration of Al(III) was established in the range 0.1–0.8 μM , being the linear regression equation $A = 0.58 + 0.05 [\text{Al(III)}]$ ($R^2 = 0.99$, $S_{yx} = 0.002$).

The current importance of trace analysis makes the setting-up of capability of detection one of the most interesting figures of merit of any analytical method. It is clear that this parameter depends not only on the probability of false positive (α values), but also on the probability of false negative (β values). Thus, it is possible to distinguish between CC_α (decision limit) and CC_β (capability of detection). CC_α may be defined as the lowest concentration level at which a method, with a statistical probability of $1-\alpha$, can discriminate if the target analyte is present in the analyzed sample. CC_β represents the lowest concentration level at a method is able to detect the presence of the analyte in a sample with a probability $1-\beta$. The decision limit and the capability of detection values obtained for the developed method were 160 and 300 nM, respectively ($\alpha = \beta = 0.05$) [52].

The precision of the method was also determined in terms of the reproducibility of the slopes obtained for different calibration sets. Three calibration curves were constructed in the concentration range from 0.1 to 0.8 μM and the relative standard deviation (RSD) value found for their slopes was 9.8 %.

3.2. Fluorescence measurements of Al(III)-morin complex

The analysis of Al(III) was also possible using a method based on fluorescence measurements. Fig. 2 shows the emission spectra of the Al(III)-morin complex in acetic-acetate medium. It can be seen that the maximum fluorescence is obtained at 505 nm. This signal was affected by different parameters including pH and morin concentration, thus, both parameters were optimized. In this way, the effect of pH was studied over a range from 2.5 to 5.9 and morin concentration in the range from 1 to 10 μM , being pH 5.0 and 10 μM the optimum values found.

In this case, the linear range of the method was established for a concentration of Al(III) from 0.1 to 1.0 μM ($E = 1.1 + 117.9 [\text{Al(III)}]$) ($R^2 = 0.99$, $S_{yx} = 37.8$). The reproducibility of the method was also estimated in terms of the RSD obtained for the slopes of three calibration curves constructed in the Al(III) concentration range from 0.1 to 1.0 μM . A good value of 2.1 % was obtained for this parameter. Finally, the decision limit and the capability of detection values obtained for the developed method were 60 and 110 nM, respectively ($\alpha = \beta = 0.05$).

3.3. Electrochemical measurements of Al(III)-morin complex

The determination of Al(III) can be performed using DPV as the analytical technique. The DPV voltammograms shown in Fig. 3 for 0.7 μM Al(III) in the absence and presence of morin prove that a complex formation reaction occurs. The anodic peak at + 0.6 V is related to the Al(III)-morin complex oxidation and can be used as the analytical response for the determination of this metal. This analytical response may be influenced by different experimental variables, such as pH and the concentration of the complexing agent. Thus, these factors were optimized in order to find the best possible analytical conditions.

Experimental design was also used as the tool for performing this optimization process through a 2^2 central composite design, taking the value of intensity recorded for a solution $2.0 \mu\text{M}$ of Al(III) as a response variable. The high (+) and low (-) levels chosen for each of the factors to be optimized were the following:

$$\begin{aligned} \text{pH} (-) &= 3.5 & [\text{morin}] (-) &= 30 \mu\text{M} \\ \text{pH} (+) &= 5.5 & [\text{morin}] (+) &= 170 \mu\text{M} \end{aligned}$$

The response surface obtained for the described experimental design showed a well-defined maximum for the oxidation current at a $146 \mu\text{M}$ concentration level of morin and a pH value of 4.4 (Figure 4). Under these optimized experimental conditions, it was observed that the oxidation current response increased after a deposition time (t_{dep}) at a fixed deposition potential (E_{dep}) (Figure 5). Therefore, the sensitivity of the developed method may be improved using adsorptive stripping voltammetry as the analytical technique. The new experimental variables (E_{dep} and t_{dep}) were also optimized by means of experimental design methodology, obtaining + 243 V and 210 s as the optimum values for E_{dep} and t_{dep} , respectively.

Under these optimum conditions the linear range of the developed method was established in the interval $0.07\text{--}13 \mu\text{M}$ ($I \text{ (nA)} = - 5.9 + 119.9 [\text{Al(III)}]$; $R^2 = 0.99$, $S_{yx} = 39.9$).

The precision of the method was also determined in terms of the reproducibility of the slopes obtained for different calibration sets. Five calibration curves were constructed in the concentration range from 70 to 630 nM and the RSD value found for their slopes was 4.6 %. Finally, the decision limit and the capability of detection values obtained for the developed method were 40 and 70 nM, respectively ($\alpha = \beta = 0.05$).

3.4. Effect of diverse ions and analysis of a real sample

Taking into account the previous results it can be concluded that the described electrochemical method led to the best results in terms of sensitivity and precision, but especially in terms of simplicity. Thus, this method was selected for the analysis of Al(III) in a real sample including a previous study of the effect of the presence of foreign ions.

Ca(II), Mg(II), Ni(II), Fe(III), Cd(II), Co(II), Pb(II), Cr(VI) and Cr(III) ions had no effect on the electrochemical determination of Al(III), even when their concentrations exceed 1000 times that of Al(III) concentration. When Zn(II) ions were introduced, no effect was observed until its concentration exceeded 100 times aluminium concentrations. In the case of Cu(II) ions, an oxidation signal was observed close to the Al(III) oxidation signal in presence of morin, causing an important interference when Cu(II) concentration exceed 10 times that of Al(III) concentration.

The proposed electrochemical method was finally applied to the practical analysis of Al(III) concentrations in three different water samples, namely river, tap and bottled water (Table 2). The standard addition method was used in all cases. The developed method resulted successfully applicable to the analysis of Al(III) in real samples taking into account the good recoveries found.

Conclusions

In this paper, a very simple, fast and sensitive electrochemical method for determination of aluminium by DPAdSV using morin as complexing agent has been developed. Compared with other previously described electrochemical procedures, this method has shown important advantages including its relative simplicity, as no working

electrode modification have been necessary and its high sensitivity and selectivity, since no serious interference has been observed. Moreover, it has been shown as an environmental friendly procedure because HMDE has not been longer used as working electrode.

In comparison with UV-Vis and spectrofluorimetric procedures, performed in similar experimental conditions, the electrochemical method has presented higher simplicity and greater sensitivity, being its reproducibility comparable to that of those methods.

The good agreement found between the spiked concentration values and the calculated concentration values, in the analysis of river, tap and bottled water samples, has demonstrated the efficacy of this procedure in the determination of aluminum without tedious pretreatment in complex real samples.

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Fig 1. Absorption spectra obtained for (—) [morin], 300 μM and (— —) [morin], 300 μM ; [Al(III)], 200 μM (Acetic-acetate; pH, 4.5)

Fig 2. Emission spectra obtained for (— —) [morin], 10 μM and (—) [morin], 10 μM ; [Al(III)], 1.0 μM (Acetic-acetate; pH, 4.5)

Fig 3. DPV voltammograms obtained using a GCE for (—) Blank; (— —) [morin], 150 μM and (····) [morin], 150 μM ; [Al(III)], 0.7 μM (Acetic-acetate; pH, 4.5)

Fig 4. Response surface for the 2^2 central composite design for pH and concentration of morin.

Fig 5. DPAdSV voltammograms obtained using a GCE for (— —) t_{dep} , 0; (—) t_{dep} , 120 s; E_{dep} , 0 V (Acetic-acetate; pH, 4.5; [morin], 146 μM ; [Al(III)], 0.2 μM).

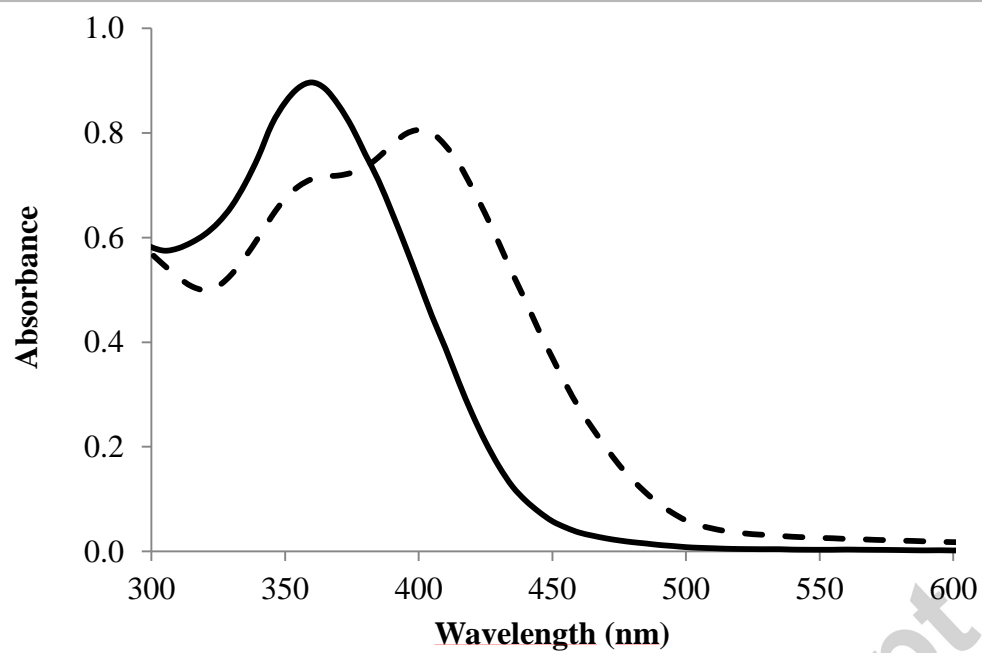


Figure 1

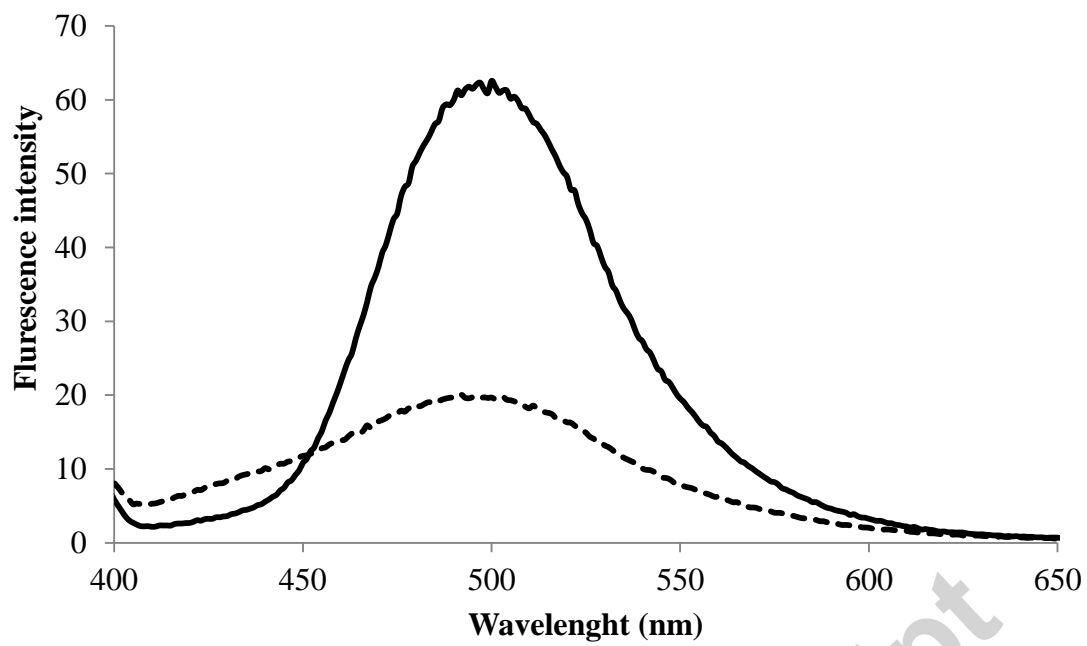


Figure 2

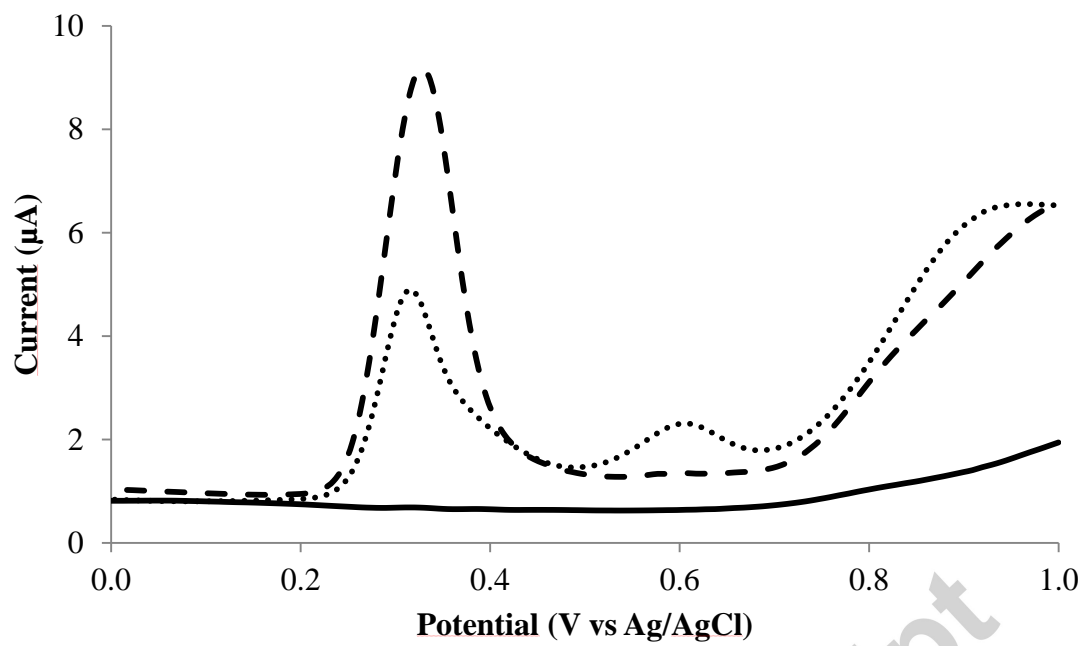


Figure 3

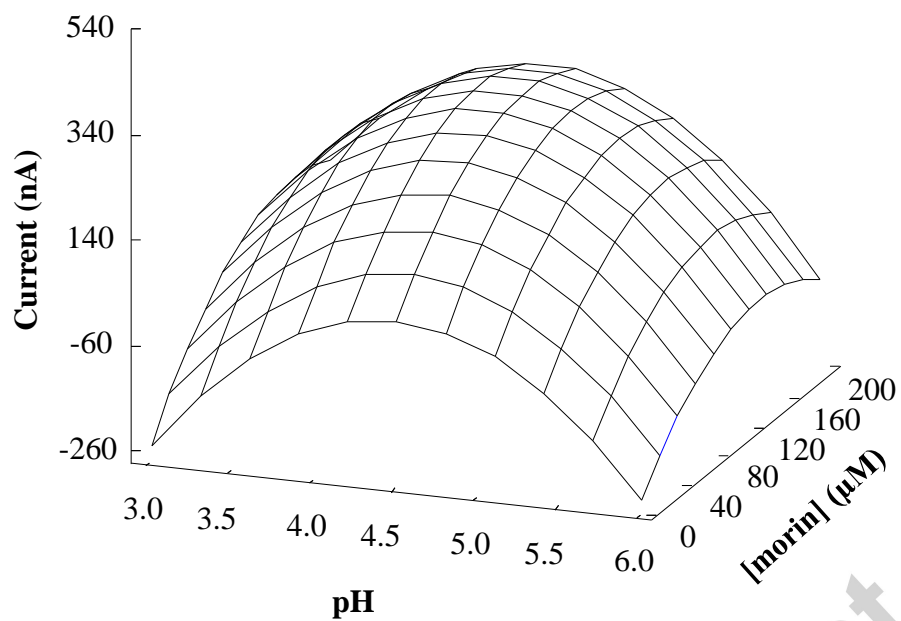


Figure 4

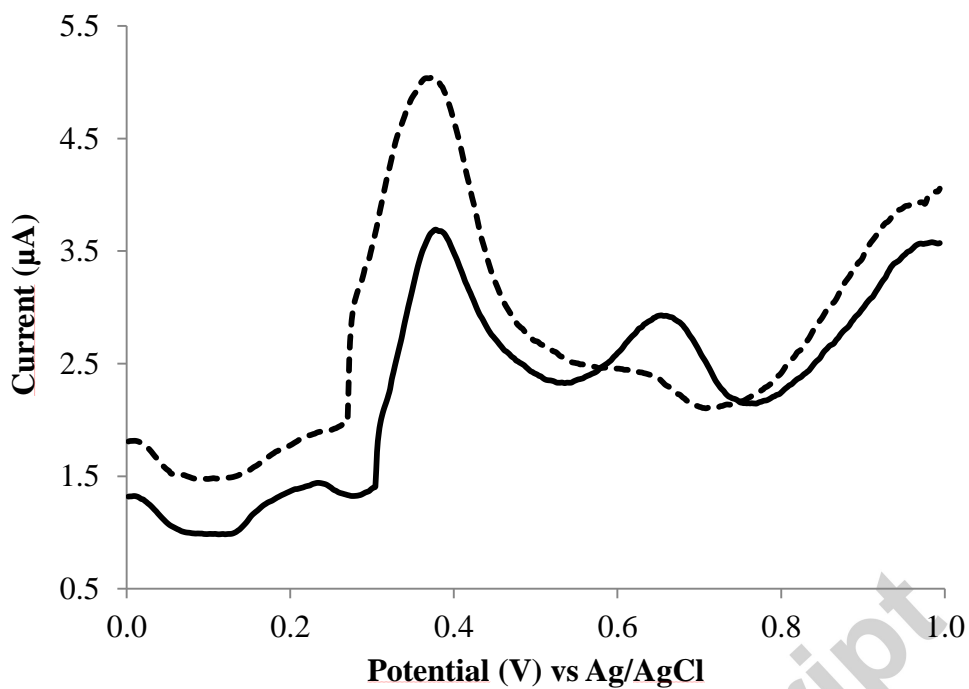
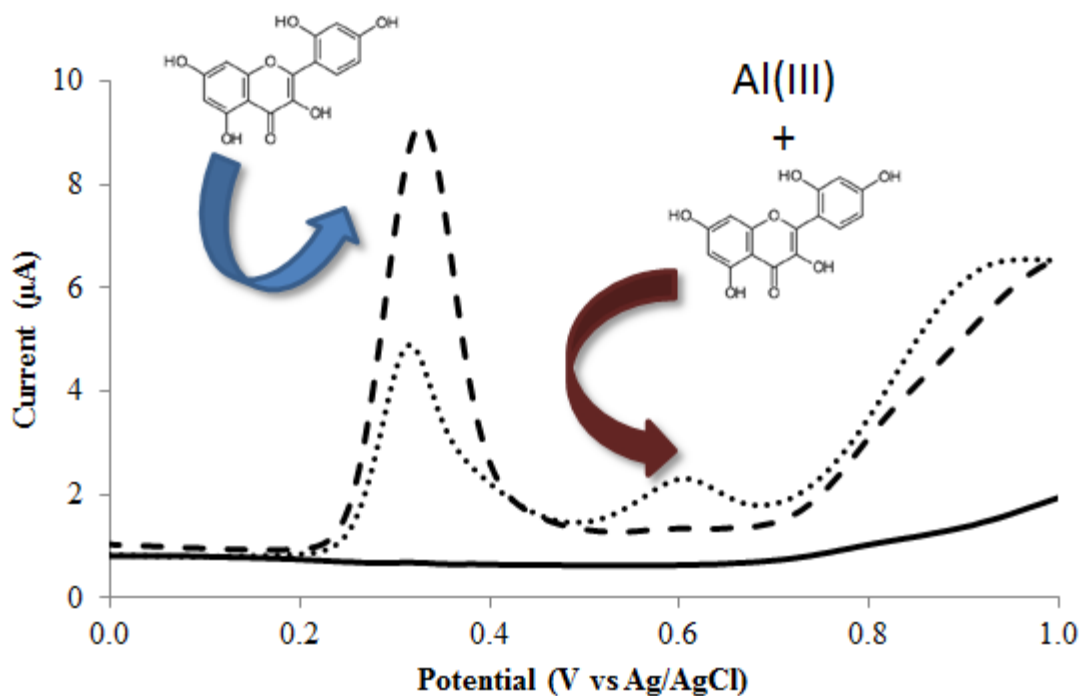


Figure 5.



Graphical Abstract

Table 1. Determination of aluminium

Technique	Complexing Agent	Limit of decision	Reproducibility (RSD)	Ref.
UV-Vis spectrophotometry	Pyrocatechol Violet	370 nM	0.1 %	[12]
		---	---	[13]
	Morin	220 nM	---	[14]
		160 nM	9.8 %	This method
	Alizarin red S	70 nM	---	[15]
	8- hydroxyquinoline	150 nM	2.4 %	[6]
	8-hydroxyquinoline-5-sulfonic acid	80 nM	0.9 %	[9]
	5,7-dibromo-8-aminolinol salicylaldehyde picolinoylhydrazone	110 nM	3.0 %	[16]
Spectrofluorimetry		9.8 nM	1.9 %	[17]
		440 nM	---	[18]
	Lumogalliom	0.7 nM	0.1 %	[19]
		0.7 nM	3.6%	[20]
		7.4 nM	3.0 %	[21]
	Morin	160 nM	2.3%	[22]
	60 nM	2.1 %	This method	

Table 1. Determination of aluminium (cont.)

Technique	Complexing Agent	Limit of decision	Reproducibility (RSD)	Ref.
		5.5 nM	---	[23]
	Solochrome violet RS	1000 nM	----	[24]
		4.5 nM	----	[25]
		1.0 nM	----	[28]
DPA _{AdSV} in HDME	Alizarin red S	----	----	[31]
		----	----	[32]
	Calmagite	37 nM	----	[35]
		----	----	[36]
	Cupferron	1.1 nM	---	[38]
	Solochrome violet RS	5.1 nM	----	[27]
		----	----	[29]
AdSV in HDME	Alizarin red S	----	----	[30]
	Alizarin	25 nM	---	[37]
	Cupferron	24 nM	3.0 %	[39]

Table 1. Determination of aluminium (cont.)

Technique	Complexing Agent	Limit of decision	Reproducibility (RSD)	Ref.
LSAdSV in HDME	Pyrocatechol Violet	3.7 nM	---	[33]
Derivative adsorption chronopotentiometry in	Pyrocatechol Violet	8 nM	---	[34]
DPP in HDME	Solochrome violet RS	110 nM	----	[26]
AdSV en SPE	Alizarin	700 nM	11.6%	[40]
DPV in GCE	Alizarin red S	0.8 nM	2.7%	[41]
	Alizarin	0.9 nM	3.2%	[42]
DPAdSV in GCE	8-hydroxyquinoline	10 nM	----	[43]
	Morin	40 nM	4.6 %	This method
LSAdSV in GCE	Cupferron	---	----	[44]
SWAdSV in GCE	Cupferron	18 nM	4.2%	[45]

AdSV: Adsorptive stripping voltammetry; DPAdSV: Differential pulse adsorptive stripping voltammetry; DPP: Differential pulse polarography; GCE: Glassy carbon electrode; HDME: Hanging drop mercury electrode; LSAdSV: Linear Scan Voltammetry after adsorptive accumulation; SPE: Screen-printed electrode; SWAdSV: Square wave adsorptive stripping voltammetry

Table 2. Determination of Al(III) in different water samples by DPVAdSV using a GCE

(N = 3)

Sample	[Al(III)] added (μM)	[Al(III)] found (μM)	Recovery
	-----	3.0 ± 0.6	-----
River water	3.0	6.5 ± 1.0	109 %
	6.0	9.1 ± 1.9	101 %
	-----	0.84 ± 0.02	-----
Tap water	0.9	1.6 ± 0.2	97 %
	1.7	2.5 ± 0.3	99 %
	-----	No detected	-----
Bottled water	0.9	0.92 ± 0.05	103 %
	1.7	1.7 ± 0.2	100 %

Highlights

- Voltammetric determination of Al(III) using a GCE.
- High sensitivity and selectivity.
- Comparison of electrochemical, UV-VIS and spectrofluorimetric methods.
- Successful determination of Al(III) in real samples.