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Simultaneous determination of iron and copper using screen-printed carbon electrodes by adsorptive stripping voltammetry with o-phenanthroline

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ABSTRACT

The simultaneous voltammetric determination of iron and copper was accomplished by an unmodified screen-printed carbon electrode based on the complexation with o-phenanthroline assisted by the reducing agent ferrocyanide. The detection limits were 3.74 and 0.34 μg L^{-1} for iron and copper, respectively, and a linear response was observed from 12.5 to 400 μg L^{-1} for iron and from 1.14 to 400 μg L^{-1} for copper. This method successfully avoids interferences between iron and copper while allowing the simultaneous determination of both low and high metal concentrations usually found in the environment. Finally, a certified wastewater reference material was successfully analyzed, confirming the precision and accuracy of the proposed method.

1. Introduction

Iron and copper are known for significantly influencing the chemical and biological processes in the environment. Their presence is not only necessary but also vital in terms of environmental cycles [1]. However, they may also cause peril for the same processes and cycles as they exhibit toxic properties at high concentrations [2,3]. Concentrations of copper and iron in the environment may vary remarkably from high levels in soils [4] and ground waters [5] to low levels in the snow [6] and seawater [7]. In drinking water, World Health Organization set certain permissible limits for iron and copper as 0.3 mg L^{-1} and 2 mg L^{-1}, respectively [8]. Therefore, it is crucial to determine and monitor their concentrations in various aqueous media such as potable waters, wastewaters, and natural waters.

Usually, multimetal determination is achieved by inductively coupled plasma with either optical emission spectroscopy (ICP-OES) or mass spectrometry (ICP-MS). However, this technique suffers from high economical cost of instrument acquisition and maintenance, and requires trained personnel. In addition, bulky instruments hinder its implementation in *on-site* analysis, requiring sampling, transport and storage of samples and thus delaying the obtention of results [9]. As an alternative, voltammetric methods overcome the main drawbacks of ICP for *on-site* analysis, providing good sensitivity and reproducibility with simpler, portable and more economical instrumentation [10]. Moreover, commercially available screen-printed electrodes (SPEs) contribute to the portability of voltammetric methods as they are compact, disposable and reproducible devices that can be easily attached to portable instrumentation [11].

Copper voltammetric determination has been widely reported in the literature using different methods and electrodes including those modified with metal films and metal nanoparticles [12–14], and chemically modified electrodes [15,16]. In contrast, voltammetric iron determination is usually regarded as challenging as demonstrated by the significantly lower amount of works available in the literature. Relevant studies demonstrate two main approaches for this purpose: (i) direct reduction of Fe(III) to Fe(II) on the working electrode and (ii) adsorptive stripping voltammetry (AdSV), which provides a higher sensitivity due to the accumulation step [17]. Accumulation in AdSV requires the presence of a suitable ligand to allow the formation of an iron complex that can be adsorbed onto the electrode surface. The most usual ligand for iron is 1,10-phenanthroline (also known as o-phenanthroline, Phen) [18], which presents a higher affinity for Fe(II) than Fe(III) (log $\beta_{3,Fe(II)-Phen} = 21.0$ and log $\beta_{3,Fe(III)-Phen} = 14.1$ [19]). However, Fe(II) is not stable and it is easily oxidized to Fe(III). Thus, to enable the complexation of Fe(II) and Phen, a prior reduction step is required. Jezek et al. [20] demonstrated that this reduction step benefits from the presence of

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a reducing agent such as ferrocyanide.

Nevertheless, the simultaneous voltammetric determination of iron and copper is usually regarded as challenging due to their interactions [21–25]. For example, a study of Matocha et al. [26] stated that Cu(II) is easily reduced to Cu(I) by Fe(II) ions, whereas Simpson et al. [27] reported that Cu(II) displaces Fe(II) from FeS and forms CuS in spiked sediments. Furthermore, considering that these metal ions are present in the environment in a wide range of concentrations, wider linear ranges for the simultaneous determination of iron and copper are required. However, most reported voltammetric methods only focused on either high [28,29] or low [30,31] concentrations. Therefore, a simple and cost-efficient method that covers a wide range of concentrations for iron and copper is deemed necessary in electroanalytical applications.

Thus, this work focuses on the development of a voltammetric method for the simultaneous determination of copper and iron via AdSV using an unmodified screen-printed carbon electrode (SPCE) in the presence of Phen as a ligand for both metal ions and ferrocyanide as a reducing agent. The proposed method overcomes two of the main issues reported in the literature for the simultaneous determination of these metal ions: (i) it is suitable for a wide range of concentrations that covers both high and low concentrations (from very low to hundreds μg L^{-1}) found in environmental scenarios and (ii) it is not affected by Fe-Cu interactions that often hinder their simultaneous determination. Moreover, in the scope of this study, reported data from relevant studies that dealt with simultaneous determination of iron and copper is also presented (Table 1). The main advantage of the proposed method over previous works is that it is able to determine both metals in a large linear range without needing any complicated electrode modification procedure or using non-environmentally friendly materials.

2. Experimental

2.1. Chemicals

All chemicals used in this study were of analytical grade. o-phenanthroline (Phen) was purchased from J.T. Baker (Pennsylvania, USA), $K_4Fe(CN)_6$ was supplied by Panreac (Barcelona, Spain) and all other products were acquired from Merck (Darmstadt, Germany). Stock solutions of Cu(II) and Fe(III) were prepared from their salts and standardized complexometrically. All solutions were prepared with water obtained from Milli-Q Reference A + Water Purification System (Millipore, France) with an electrical resistivity of 18.4 MΩ. Certified wastewater reference material (SPS-WW2, Waste Water Level 2, Batch no: 112) was obtained from Spectrapure Standards AS (Oslo, Norway). The certificate of analysis provided by the producer states that this reference material contains 13 elements with the following concentrations: 10000 μg L^{-1} Al, 500 μg L^{-1} As, 100 μg L^{-1} Cd, 300 μg L^{-1} Co, 1000 μg L^{-1} Cr, 2000 μg L^{-1} Cu, 5000 μg L^{-1} Fe, 2000 μg L^{-1} Mn, 5000 μg L^{-1} Ni, 5000 μg L^{-1} P, 500 μg L^{-1} Pb, 500 μg L^{-1} V, 3000 μg L^{-1} Zn. All reagents and prepared solutions were stored at + 4 °C until their use.

2.2. Voltammetric measurements

Voltammetric measurements were carried out via the NOVA 2.1.3 (Metrohm Autolab, Utrecht, Netherlands) electrochemical software system, and employing an Autolab PGSTAT204 Potentiostat/Galvanostat by Metrohm (Utrecht, Netherlands). Electrochemical procedures were conducted at room temperature and without dearation with a three electrode system that consisted of Ag/AgCl/KCl (3 mol L^{-1}) reference electrode, a Pt counter electrode from Metrohm, and a working carbon electrode with 4 mm diameter from a screen-printed carbon electrode (SPCE) supplied by Metrohm DropSens (DRP-110, Spain).

Voltammetric measurements were carried out in a solution containing 0.1 μmol L^{-1} $K_4Fe(CN)_6$ and 100 mg L^{-1} Phen in acetate buffer (pH 4.5). Metal accumulation was performed by applying a deposition potential (E_d) of −0.4 V for 240 s under constant stirring. The oxidation step takes place from −0.4 V to 1.0 V with 0.05 s modulation time, 2 mV step potential, and 50 mV modulation amplitude. A new SPCE was employed for every experiment and three repetitive blank measurements were initially taken in order to obtain a stable background current. Blank correction was applied in all measurements.

Certified wastewater reference material was analyzed using the standard addition calibration method. pH was adjusted in the vessel by the addition of pH 4.5 acetate buffer, resulting in a dilution factor of 1/20; then Phen and ferrocyanide were added and voltammetric measurements were carried out at the above-mentioned conditions. Three successive metal additions were performed and the corresponding voltammograms were recorded.

3. Results and discussion

Fig. 1 shows a tentative mechanism for the AdSV determination of iron and copper assisted by Phen and ferrocyanide. In the stripping step a deposition potential of −0.4 V is applied for 240 s, resulting in a two-step process. Initially Fe(III) and Cu(II) are reduced to Fe(II) and Cu(I), respectively with the aid of $K_4Fe(CN)_6$. Next, Fe(II) and Cu(I) are complexed with the Phen present in solution and adsorbed onto the electrode surface. It is worth noting that the presence of $K_4Fe(CN)_6$ as reducing agent is imperative for the AdSV iron determination whereas the reduction of Cu(II) is possible without the presence of ferrocyanide, albeit to a slightly lower extension. Then, during the anodic scan, the oxidation of Fe(II)-Phen and Cu(I)-Phen complexes is recorded, showing two oxidation peaks at *ca.* −0.2 V and 0.8 V for copper and iron, respectively, as well as a third signal at *ca.* 0 V related to the oxidation of ferrocyanide from the solution (Fig. 2).

3.1. Optimization of complex formation conditions and voltammetric parameters

As a first step, the parameters related to the stripping step were optimized to ensure the proper reduction of Fe(III) and Cu(II). Fig. 2a

Table 1
Reported findings from studies that investigated simultaneous voltammetric analysis of iron and copper.

Ref	Electrode	Analyte	Technique	Deposition time	Applied samples	Peak potentials (V)		LOD (μg L^{-1})		Linear range (μg L^{-1})	
						Cu	**Fe**	**Cu**	**Fe**	**Cu**	**Fe**
[31]	B-doped diamond electrode	Fe, Cu, Zn, Pb, Cd	SWASV	60 s	Fuel ethanol	0.05	0.53	1.42	1.9	2–40	2–40
[32]	HMDE	Fe, Cu, Cd	DPAdSV	60 s	Tap water	−0.28	−0.46	0.4	0.5	0.5–100	1–80
[33]	HMDE	Co, Cu, Fe, Ni, V	AdCSV	60 s/300 s [a]	Estuarine pore water	−0.18	−0.35	0.006	0.07	Up to 5.08	Up to 16.8
[34]	N/CNT/GCE	Fe and Cu	LSSV	270 s	Fuel ethanol	0.05	0.50	3.2	40	6.4–57	56–2792
[35]	CPE	Mn, Cu, Fe	SWAdCSV	240 s	Ground, tap, and bottled water	−0.05	−0.36	0.11	0.09	0.36–45	0.31–25
This study	Bare SPCE	Fe and Cu	DPAdSV	240 s	Wastewater CRM	−0.20	0.76	0.34	3.74	1.14–400	12.5–400

Abbreviations: B, Boron; SWASV, square wave anodic stripping voltammetry; HMDE, hanging mercury drop electrode; DPAdSV, differential pulse adsorptive stripping voltammetry; N, Nafion; CNT, carbon nanotube; GCE, glassy carbon electrode; LSSV, linear sweep stripping electrode; CPE, carbon paste electrode; SWAdCSV, square wave adsorptive cathodic stripping voltammetry; AdCSV, adsorptive cathodic stripping voltammetry; SPCE, screen printed carbon electrode.

[a] 300 s of deposition for LOD and 60 s deposition for linear range calculation.

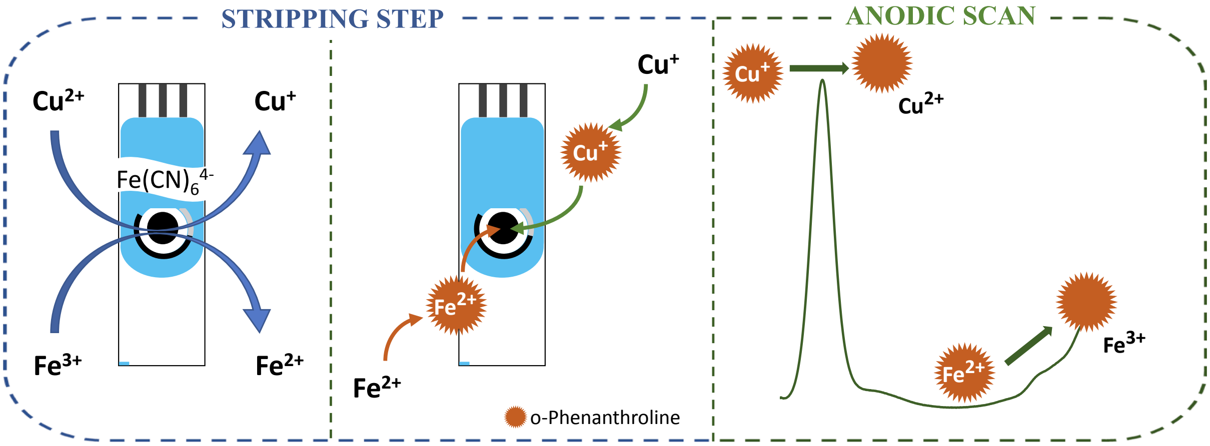

Fig. 1. Schematic description of suggested mechanism for iron and copper reduction on the electrode surface assisted by o-phenanthroline and ferrocyanide.

displays the effect of $K_4Fe(CN)_6$ concentration on the AdSV determination of iron and copper. As it can be seen, increasing concentrations of $K_4Fe(CN)_6$ give rise to higher voltammetric peaks for both metal ions. This is in agreement with the above-proposed mechanism as higher concentrations will lead to a more effective reduction of Fe(III) and Cu (II). However, large concentrations of $K_4Fe(CN)_6$ result in an excess of ferrocyanide that is also oxidized in the anodic scan, showing a voltammetric peak at *ca.*0.05 V that partially overlaps with copper peak. Thus, 0.1 µmol L^{-1} of $K_4Fe(CN)_6$ was selected as a compromise concentration for further measurements.

Deposition potential and time were also optimized considering E_d from −0.4 V to −0.6 V and t_d from 120 to 360 s. An E_d of −0.4 V provided the largest peaks for both analytes and a t_d of 240 s was selected as a compromise between peak current and time analysis.

Then, in order to improve the formation of metal ion complexes, Phen concentration and pH were also optimized. Three different concentrations were tested for Phen: 10, 100, and 1000 mg L^{-1}. As it can be seen in Fig. 2b, high concentrations of Phen result in higher copper voltammetric peaks but lower iron peaks. In addition, the peak related to the oxidation of ferrocyanide considerably increases at high Phen concentrations. This fact can be explained because high amounts of Phen hinder the reduction of Fe(III) to Fe(II), even in the presence of $K_4Fe(CN)_6$. As a consequence, iron peak decreases and ferrocyanide is not consumed, leading to a higher oxidation peak.

Finally, pH is also a crucial parameter because it affects the complexation process. pH values from 2.0 to 4.5 were evaluated (Fig. 2c). For this purpose, several buffers were prepared: acetate buffer (pH 3.75 – 4.50), citrate buffer (pH 2.75 – 3.25) and hydrochloric acid (pH 2). Higher pH was not considered to avoid the formation of hydroxocomplexes, which is particularly important in the case of iron. The highest and best-defined voltammetric peaks were achieved at pH 4.5. Lower pH values lead to the protonation of Phen (pK_a = 4.27), which hinders the complexation process.

3.2. Analytical performance

Once the optimal conditions for the determination of copper and iron were established, both individual (Fig. 3) and simultaneous (Fig. 4) calibrations of target metal ions were carried out considering concentrations from 0.5 to 400 and from 5 to 400 µg L^{-1} for copper and iron, respectively. Each calibration study was conducted in triplicate and their average values and standard deviations were computed. A large and well-defined oxidation peak was observed for copper, whereas the voltammetric peak of iron is much lower. This could be due to the positive charge of both Cu(I) and Fe(II) complexes with Phen. Although both of them are accumulated onto an electrode submitted to a negative potential, the adsorbed complex of copper is reoxidized at a slightly less negative potential, which ensures that it remains at the electrode surface until it is stripped from it. In contrast, the oxidation of the adsorbed Fe (II)-Phen complex takes place at a very positive potential (due to the higher stability as compared to the complex of Fe(III)) and electrostatic repulsion may cause a desorption of most of the accumulated complex

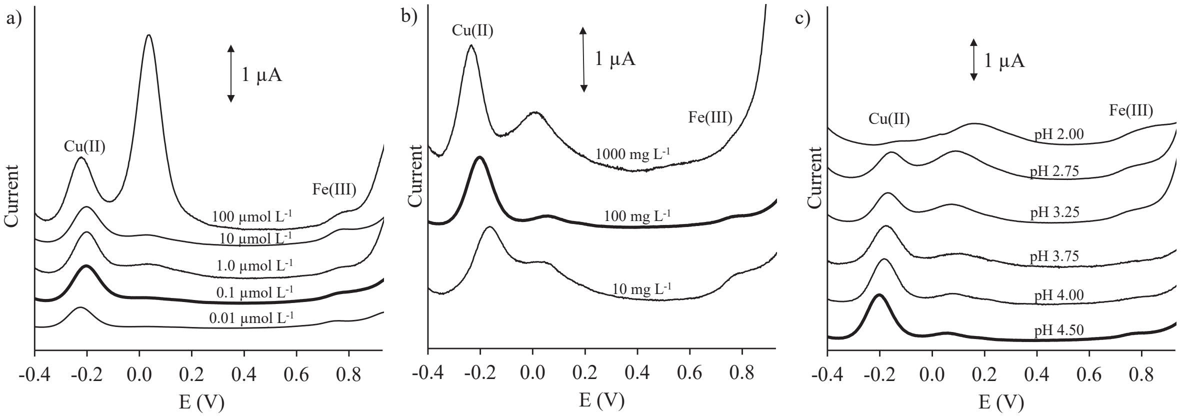

Fig. 2. Optimization of complex formation conditions: (a) concentration of $K_4Fe(CN)_6$, (b) concentration of o-phenanthroline, and (c) pH. Optimization was always performed using a solution containing 50 µg L^{-1} of Cu(II) and either 100 (for a) or 50 (for b and c) µg L^{-1} of Fe(III) and applying an E_d of −0.4 V for 120 s. Concentration of o-phenanthroline was fixed to 100 mg L^{-1} in (a) and (c); pH was set to 4.5 in (a) and (b) and 2 µmol L^{-1} $K_4Fe(CN)_6$ was employed in (b) and (c).

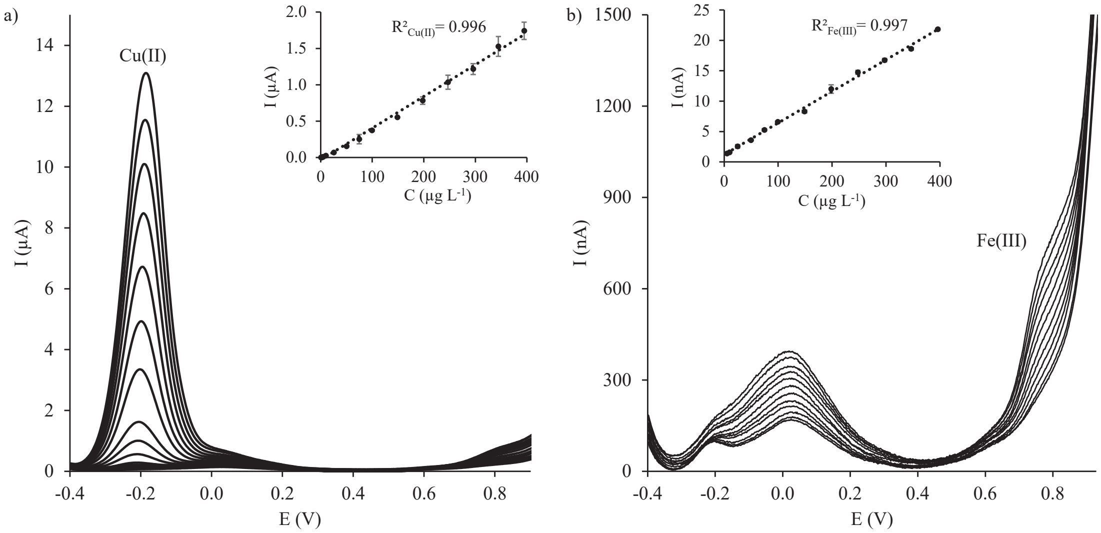

Fig. 3. Individual calibration plots and corresponding calibration curves (insets) of (a) Cu(II) and (b) Fe(III) in pH 4.5 acetate buffer acquired by applying an E_d of −0.4 V for 240 s in the presence of 0.1 µmol L^{-1} $K_4Fe(CN)_6$ and 100 mg L^{-1} o-phenanthroline.

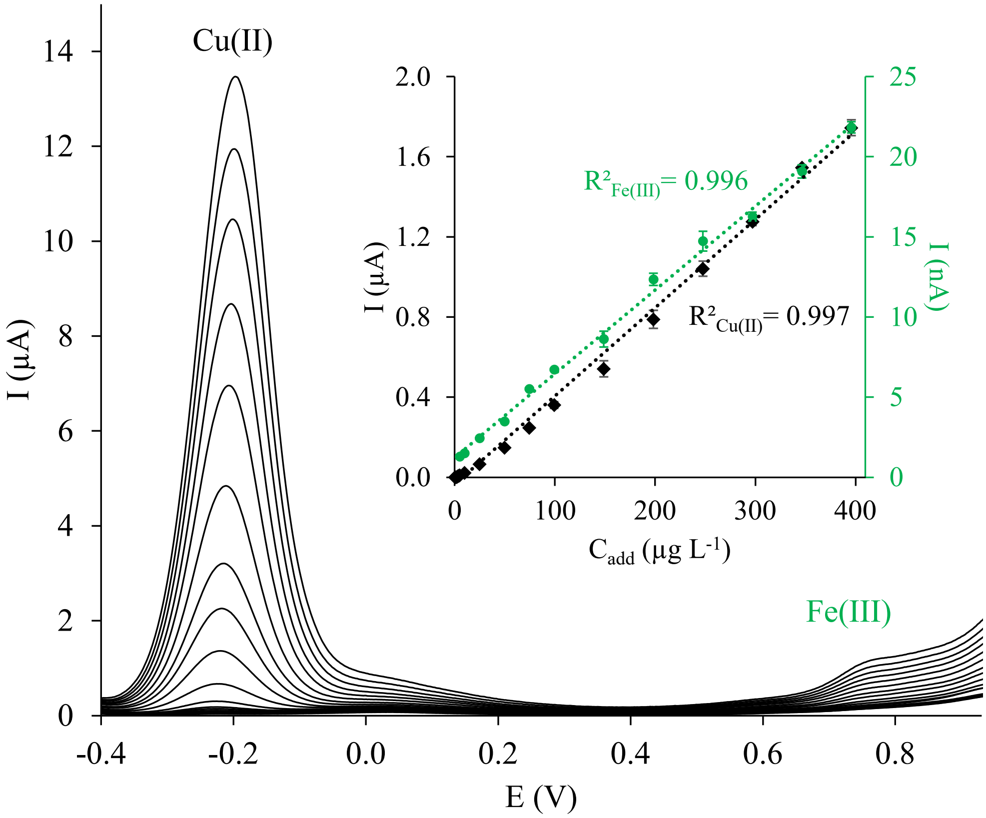

Fig. 4. Simultaneous calibration voltammograms of Cu(II) and Fe(III) acquired by applying an E_d of −0.4 V for 240 s, in the presence of 0.1 µ mol L^{-1} $K_4Fe(CN)_6$ and 100 mg L^{-1} o-phenanthroline in pH 4.5 acetate buffer. Inset: Calibration curves for Cu(II) (diamond, black) and Fe(III) (round, green).

before it can be reoxidized. Anyway, as it will be explained later, the remaining adsorbed iron is enough to provide an acceptable sensitivity. Moreover, both peaks increase linearly with metal ion concentration as it can be observed in the calibration plots (insets in Figs. 3 and 4).

The analytical performance was assessed in terms of sensitivity (as the slope obtained from the calibration curves), linearity and limits of detection (LOD) and quantification (LOQ) (Table 2). LOD and LOQ were calculated as 3σ/s and 10σ/s, respectively, where "σ" represents the standard deviation of the y-intercept and "s" represents the slope attained from the lower part of the corresponding calibration curves (0.5–25 μg L^{-1} for copper and 5–100 μg L^{-1} for iron). LOQ was stated as the lower limit of the linear range.

As expected from the obtained AdS voltammograms, copper sensitivity is much higher than that observed for iron. According to the previous discussion, this could be attributed to copper complex being more easily accumulated and retained on the electrode surface until reoxidation. Moreover, the sensitivities achieved in both individual and simultaneous calibration were mainly the same, which indicates that iron and copper do not interfere with each other during simultaneous measurements. It should be highlighted that previous works dealing with the determinations of iron and copper reported important problems associated to these interactions [24,25,36,37]. We hypothesize that the lack of interactions in this method could be attributed to the presence of the reducing agent $K_4Fe(CN)_6$, which reduces both Fe(III) and Cu(II), preventing the coexistence of Fe(II) and Cu(II) and avoiding redox processes among them. Thus, the lack of interaction between iron and copper represents a significant improvement in the simultaneous voltammetric determination of these metal ions.

A good linearity up to 400 μg L^{-1} was achieved for both metal ions, providing a wide linear range that covers both low and high concentrations expected in the environment. This fact is a strong point of this method as the majority of works reported in the literature mainly deal with either low concentrations [25] or large concentrations [29], particularly in the case of iron. Moreover, linear ranges were not altered in the simultaneous calibration, demonstrating that iron and copper are not competing for the working electrode surface and again confirming the lack of interaction between both species.

LODs and LOQs from individual and simultaneous calibrations are summarized in Table 2. As it can be seen, LODs around 0.3 and 3.7 μg L^{-1} were achieved for copper and iron, respectively. It should be highlighted that LODs were practically the same in separate and joint calibrations, confirming the suitability of this method for the simultaneous determination of iron and copper.

The analytical performance reported in the present study was also compared to other relevant studies in the literature that investigated simultaneous iron and copper determination via voltammetric methods. This comparison is revealed in Table 1. Ferreira *et al.* reported a boron-doped diamond electrode [31] which was able to determine 5 metals simultaneously in a short deposition time. Obtained LODs were slightly lower and slightly higher than those achieved in our study for copper and iron, respectively. However, this worked focused only in low metal ion concentrations, reporting narrow linear ranges (up to 40 μg L^{-1}) with the additional drawback that diamond electrodes are highly expensive as compared to the disposable SPCE employed in this study. On the other hand, lower LOD values, particularly for iron, were reported with hanging mercury drop electrode (HMDE) [32,33], yet the extremely low values reported in the work of Santos-Echeandia [33] were achieved using a longer deposition time and were associated to a really narrow linear range. Even though HMDE is known for its exceptional performance, the concerns regarding its toxicity cause the recent trends in electrochemistry to lean toward greener alternatives [38]. As for the carbon nanotubes modified glassy carbon electrode [34], although the linear range of iron is much wider than that obtained in our method, the LOD values for both Cu and Fe are one order of magnitude higher, with the additional disadvantage of using an electrode modified with carbon nanoallotropes that increases the economical cost. Lastly, in the work of Ghoneim [35], remarkably low LOD values were obtained with a carbon paste electrode (CPE) when determining copper and iron as complexes of 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol. This work of Ghoneim seems to adopt a similar approach to our proposed method by using an unmodified electrode and adding the ligand directly into the measurement solution. Despite its simplicity, the drawback of their method is that it only allows detection at trace levels of analytes within a relatively narrow linear range, whereas copper and iron can be found at various concentration levels in the environment.

Table 2
Comparison of the analytical performances obtained with individual and simultaneous determination of Cu(II) and Fe(III) ions. Analytes were determined using E_d of −0.4 V for 240 s in the presence of 0.1 μmol L^{-1} $K_4Fe(CN)_6$ and 100 mg L^{-1}o-phenanthroline in pH 4.5 acetate buffer. The standard deviations are shown within brackets. (n = 3).

	Individual		Simultaneous	
	Cu(II)	Fe(III)	Cu(II)	Fe(III)
Sensitivity (nAV μg^{-1} L)	4.35 (0.06)	0.0521 (0.0006)	4.40 (0.04)	0.0523 (0.0006)
Intercept (μg L^{-1})	−30 (10)	1.2 (0.1)	−34 (8)	1.2 (0.1)
Linear range[a] (μg L^{-1})	1.05–400	12.4–400	1.14–400	12.5–400
R^2	0.996	0.997	0.997	0.996
LOD (μg L^{-1})	0.315	3.71	0.341	3.74

[a] The initial value of linear range is established from the calculated LOQ.

Due to the wide linear range obtained for copper and iron, repeatability and reproducibility were evaluated at two different concentration levels (50 and 250 μg L^{-1}) of both analytes to make sure that the proposed method provides satisfying repeatability and reproducibility throughout the whole concentration range. Repeatability was calculated from the relative standard deviation (RSD%) of five readings taken from a single electrode and presented as intervals to incorporate the results obtained for three different electrodes. On the other hand, reproducibility was computed from five repetitive measurements taken from three different electrodes. From the repeatability and reproducibility results presented in Table 3, it can be deduced that the method provided satisfying repeatability and reproducibility with less than 7 and 5% RSD for copper and iron, respectively.

3.3. *Certified reference material measurement*

The suitability of the developed method for the simultaneous determination of copper and iron in real samples was assessed through the analysis of a wastewater reference material using the standard addition method and in triplicate. Fig. 5a shows the obtained AdS voltammograms, which display a similar voltammetric behavior as that observed in synthetic samples. Calibration plots for copper and iron are presented in Fig. 5b and 5c, respectively and the determined concentrations are reported in Table 4. As it can be seen, good reproducibility and excellent accuracy (relative errors equal or lower than 1%) were attained for both metal ions.

Thus, these good values, coupled to the well-defined peaks obtained, show that the proposed method performs well even in a complex sample medium that also contains other ions at high concentrations (see experimental section for detailed values).

4. Conclusions

The present work deals with the simultaneous voltammetric determination of copper and iron using an unmodified and commercial screen-printed carbon electrode. This method is based on metal complexation with o-phenanthroline assisted by the reducing agent

Table 3
Results obtained from repeatability and reproducibility studies. Analytes were determined by using E_d −0.4 V for 240 s deposition time in the presence of 0.1 μmol L^{-1} $K_4Fe(CN)_6$ and 100 mg L^{-1} o-phenanthroline in pH 4.5 acetate buffer.

	Repeatability (%)		Reproducibility (%)	
	Cu(II)	Fe(III)	Cu(II)	Fe(III)
50 μg L^{-1}	2.5–4.3	1.5–2.6	2.7	3.5
250 μg L^{-1}	2.4–6.8	2.3–3.7	2.8	4.8

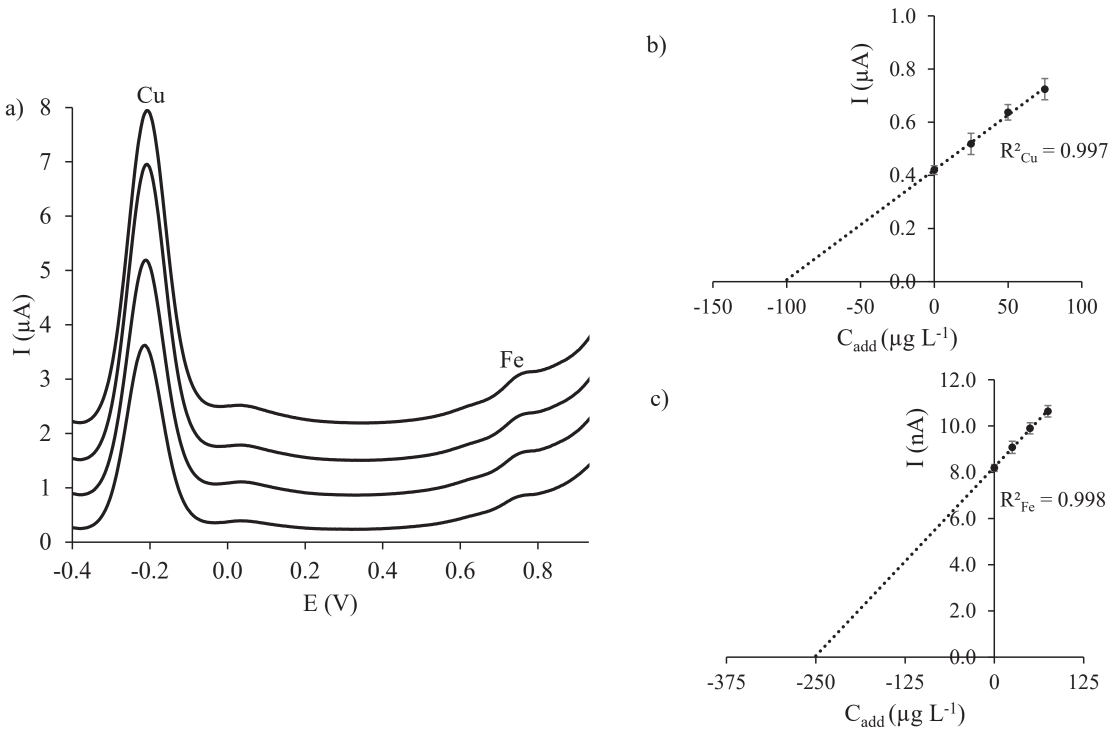

Fig. 5. Simultaneous determination of copper and iron in wastewater reference material via the standard addition method in pH 4.5 acetate applying an E_d of −0.4 V for 240 s. Voltammetric measurements were carried out in the presence of 0.1 μ mol L^{-1} $K_4Fe(CN)_6$ and 100 mg L^{-1}o-phenanthroline. Corresponding calibration plots of copper and iron are shown in (b) and (c), respectively.

Table 4
Certified and measured concentrations of copper and iron ions in the wastewater reference material. Analytes were determined using E_d of −0.4 V for 240 s in the presence of 0.1 μmol L^{-1} $K_4Fe(CN)_6$ and 100 mg L^{-1}o-phenanthroline in pH 4.5 acetate buffer. The standard deviations are shown within brackets. (n = 3).

	Certified values (μg L^{-1})	Measured values (μg L^{-1})	Relative error (%)
Cu	2000 (10)	2020 (10)	1.0
Fe	5000 (25)	5030 (60)	0.6

ferrocyanide. Individual and simultaneous calibrations were carried out and by comparing the analytical performance among them, it can be inferred that iron and copper do not interfere with each other during simultaneous measurements as their detection limits, linear ranges and sensitivity parameters were not significantly altered. Another advantage of this method is that it is suitable for the determination of both low and high concentrations of metal ions, which is of great concern in environmental analysis. Moreover, this is a simple method that does not require any complicated electrode modification process, which significantly decreases analysis time and cost. Detection limits as low as 3.74 and 0.34 μg L^{-1} were attained for iron and copper, respectively, during their simultaneous determination. It is remarkable that the method is quite more sensitive for copper than for iron. This is very appropriate for most water samples, which usually contain far more iron than copper. Quantification of both metals in certified reference material was successfully performed and both metals were accurately determined in a complex wastewater medium. Nonetheless, it should be stressed that there are very few studies that investigate the simultaneous voltammetric analysis of copper and iron. Hence, the present study not only improves some of the existing methods but also contributes to a gap in the literature.

Credit authorship contribution statement

Gul Sirin Ustabasi: Methodology, Formal analysis, Investigation, Writing – original draft, Visualization.

Clara Pérez-Ràfols: Conceptualization, Methodology, Formal analysis, Writing – original draft, Visualization, Supervision, Resources.

Núria Serrano: Conceptualization, Methodology, Formal analysis, Writing – original draft, Visualization, Supervision, Resources.

José Manuel Díaz-Cruz: Methodology, Formal analysis, Validation, Writing – review & editing, Visualization, Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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