



(RESEARCH ARTICLE)



Didactic experiment for voltametric determination the complexing capacity of natural waters

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World Journal of Advanced Engineering Technology and Sciences, 2024, 11(01), 337-344

Publication history: Received on 13 January 2024; revised on 24 February 2024; accepted on 26 February 2024

Article DOI: <https://doi.org/10.30574/wjaets.2024.11.1.0069>

Abstract

The titration method can be applied to determine the complexation capacity between metal ions and ligands in natural water samples. The process involves the incremental addition of the metal to the sample containing a specific ligand, resulting in a titration curve that reflects the formation of complexes. The change in the curves slope indicates the saturation of the complexation capacity. In this study, the copper (II) ion was used due to its stability with organic ligands. The titration curve was analyzed to determine the complexation capacity (CC) and conditional formation constant (K) of the complex. Different mathematical treatments are proposed for this analysis. In the described experiment, differential pulse anodic stripping voltammetry was used to determine the complexation capacity of humic substances in natural waters. Experimental parameters such as pH, supporting electrolyte concentration, and volume of additions were previously optimized for the voltammetry technique. The obtained data were processed and analyzed, resulting in titration curves and voltammograms. The analysis of the curves allowed for the calculation of the complexation capacity and conditional stability constant of the formed complex. The results demonstrate the feasibility of the method as a didactic experiment for the voltammetric determination of natural water complexation capacity.

Keywords: Natural Waters; Voltammetry; Complexation Capacity; Formation Constant

1. Introduction

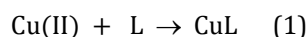
In natural water samples containing a single ligand L, which forms with metal ions M a complex ML with 1:1 stoichiometry, if M is added in small increments and, after each addition, the equilibrium concentration of the free metal ion (M) present in solution is determined, a titration curve can be obtained. There is an increase in the ML concentration as a result of the complexation of the free metal with the ligand.

A marked change in the slope of the titration curve occurs when the concentration of the metal ion is equivalent to that of the ligand. Beyond this point, the complexation capacity of the metal by the ligand will be saturated and the slope of the upper part of the titration curve is identical to the slope of the titration curve obtained when no ligand is present. The overall shape of the titration curve indicates the extent and nature of sample complexation [1].

The copper (II) ion is commonly used in titrations of surface water samples, because it forms more stable complexes with organic ligands [2].

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According to Guibaud et al. [3], different algebraic and graphical treatments of titration data to evaluate metal complexation parameters can be used. One proposal is that the complex formed between a copper (II) metallic ion and the organic matter dissolved in the water during the titration is 1:1. A simplified reaction equation can be established as:



With a conditional formation constant:

$$K = \frac{[\text{CuL}]}{[\text{Cu(II)}] \cdot [\text{L}]} \quad (2)$$

On what:

[L] is the concentration of organic matter dissolved in water capable of forming complexes with the copper (II) ion;

[Cu(II)] is the concentration of non-complexed copper (II) ion, which includes all labile copper (II) species detectable by the technique used, that is, aqueous ions and inorganic complexes;

[CuL] is the concentration of the copper (II) ion complex with the L ligand.

As illustrated in Figure 1, the titration curve presents two straight lines with well-defined slopes: the one with the smallest angular coefficient (α) corresponds to the complexation of the free metal with the ligand up to the point where the concentration of the metal is equivalent to that of the ligand, according to equation (1); the one with the highest angular coefficient (β) indicates the presence of excess copper (II) ion after the end point. The intersection of both straight lines defines the complexation capacity (CC), that is, the concentration of copper (II) ion capable of forming complexes with the dissolved organic matter present in the water sample.

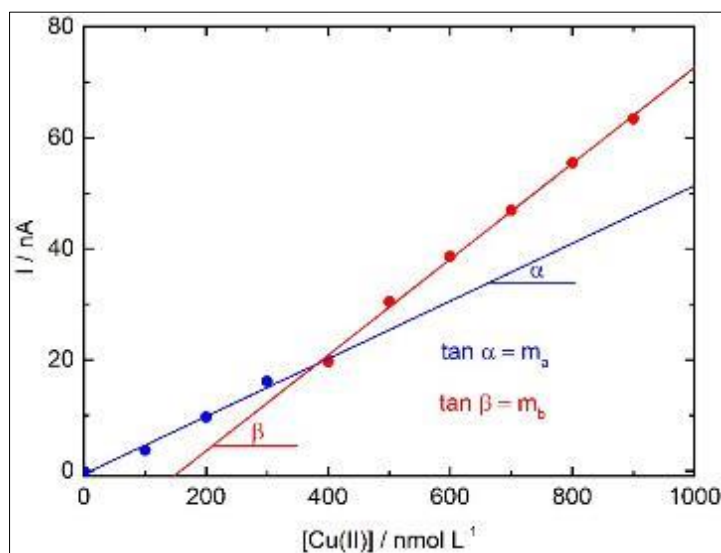


Figure 1 Titration curve model of the copper (II) ion with a ligand L.

The value of K can be obtained through the slopes (m_a and m_b) and the intersection of the two straight lines (CC) of the titration curve, according to expression (3):

$$K = \frac{m_b - m_a}{m_a \cdot \text{CC}} \quad (3)$$

It is important to note that stability constants derived from metal titration procedures are conditional and depend on certain sample parameters, such as fixed pH, ionic strength, main ion composition, and concentration of competing metals. They are not true thermodynamic constants. The stability constant values obtained are only strictly applicable to the quantities of metals used in the titration. Ligand concentration is also a conditional measurement. Titration with

a metal of interest can lead to dissociation of weaker complexes formed by the ligand with other metals. This can be an important consideration in toxicity studies, in which complexed metals can produce toxic effects different from those produced by the free metal under study.

Morrison and Florence [4] compared several techniques for measuring the complexation capacity of copper with natural and synthetic organic ligands in fresh waters. They found that analyzes by anodic redissolution voltammetry with suspended drop mercury electrodes, or mercury thin film electrodes, presented values more than an order of magnitude below the values obtained by other techniques. A widely accepted supposed explanation is that anodic redissolution voltammetry measures the concentration of labile metal rather than just the free metal. Therefore, many results obtained by anodic redissolution voltammetry measurements depend on the nature of the ligands in the system.

What happens, therefore, is that during the pre-concentration step not only the free metal ion is deposited, but also the fraction resulting from the dissociation of the complex. Electrochemical lability is measured by the susceptibility of the complex to contribute to the metal deposition current. It depends on several factors, such as the dissociation constant of the complex, the diffusion coefficients of the metal and the complex and the time scale of the experiment [5].

Differences, in voltammetric measurements, of concentrations of various ligands are often attributed to the adsorption of humic substances on the electrode surface, it may also be due to incorrect diffusion coefficient values used in speciation calculations. The diffusion coefficient of metal-humic substance complexes is a function of pH and, in certain pH ranges, the mobility of humic species increases with increasing pH. The anodic redissolution voltammetry technique is affected by the adsorption of polymeric organic ligands on the mercury droplet electrode, which can act as a hydrophobic surface to bind to non-polar organic matter [6, 7, 8].

In this sense, a didactic experiment based on differential pulse voltammetry with anodic redissolution is proposed to determine the complexation constant of humic substances present in natural waters, against metallic ions, using in this case micro additions of copper (II).

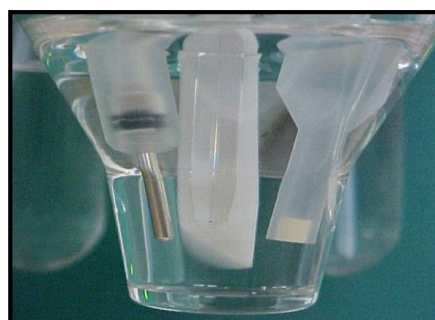
2. Material and methods

The parameters of the voltammetric analyzes were obtained from determinations and optimizations carried out by Custódio [9] and Dutra et al. [10]. After some tests of the conditions already established, the best conditions were reached for the current set of samples. Thus, obtaining sample parameters such as the volume of the sample to be titrated, the concentration, the number and volume of each addition of the titrant solution, the pH value, volume and concentration of the supporting electrolyte, and also the instruments such as the long and short deoxygenation, equilibrium, deposition and conditioning, initial, final, deposition and conditioning potentials, pulse amplitude and sweep increment.

The determinations were carried out on a VA Computrace voltammetric analyzer, model 797, from Metrohm (Figure 2a). Using a mercury hanging drop electrode (HMDE) as the working electrode, a silver/silver chloride electrode as the reference electrode, and a platinum electrode as the auxiliary electrode (Figure 2b).



(a)



(b)

Figure 2 a) 797 VA Computrace voltammetric instrument; (b) Electrode array.

The water samples were filtered using a vacuum pump, using cellulose membrane filters with a porosity of 0.45 μm , to remove suspended particles. The water samples, after being filtered, were titrated with 2.5 mg mL^{-1} copper (II) solutions, using differential pulse voltammetry with anodic redissolution as a technique.

10 mL of deionized water and 2.5 mL of supporting electrolyte (acetic acid / sodium acetate 0.1 mol L⁻¹ at pH = 4.72) were added to the voltammetric cell to scan the blank. After washing the voltammetric cell, 10 mL of natural water sample and 2.5 mL of supporting electrolyte were added and the sample was scanned and. Then, ten additions of 25 mL of 2.5 mg mL⁻¹ copper (II) solution were made sequentially, with the aid of a micropipette.

The voltammetric data were recorded using the Methrom potentiostat program, model 797 VA Computrace. This data was processed by commercial programs that operate within the Windows environment, such as Origin [11].

3. Results and discussion

After carrying out the tests with the conditions already established by Custódio [9], other necessary adjustments were made, as already mentioned, and the best conditions are shown in tables 1 and 2 (Dutra et al. [10]).

The 797 VA Computrace potentiostat data file acquired in ASCII format presents textual and numerical information. In addition to various information about experimental conditions, the file also presents numerical data arranged in two columns. In the first, the potential range is always repeated for each voltammogram obtained, while the current data is reported in the second column (Figure 3).

Each set of data relating to a voltammogram with 591 values of potential and current lines is separated by alphanumeric information.

This way, it is possible to read this data file in different programs. The Origin program, as an example, allows you to read these files and they can be worked on in matrix form and, later, presented globally in graphical form.

Table 1 Sample parameters used in voltammetric titrations

Sample	Natural water	10 mL	---
Support Electrolyte	H ₃ CCOOH/H ₃ CCONa pH = 4.72	2.5 mL	0.1 mol L ⁻¹
Titrant Solution	Copper (II)	10 additions of 25 µL	2.5 µg mL ⁻¹

For a graphical visualization of data from a voltammetric titration, in which several successive micro volumetric additions of a titrant agent are made, it is necessary to arrange these data obtained in a file in numeric matrix format. In this arrangement, the number of lines must be in accordance with the potential range explored, taking into account the initial and final potential and the number of points in each voltammogram. Furthermore, the number of columns must be in line with the number of micro volumetric additions of the titrant. In this way, the sequence of tasks performed in the Origin program aims to facilitate this change of the data file, for the graphical presentation of voltammograms.

Table 2 Instrumental parameters used in voltammetric titrations.

Parameters	Values
Long deoxygenation time	300 s
Shortt deoxygenation time	120 s
Equilibrium time	30 s
Deposition time	60 s
Conditioning time	0 s
Starting potential	- 0.15 V
Final potential	+ 0.15 V
Deposition potential	- 0.15 V
Conditioning potential	+ 0.15 V
Pulse height/amplitude	50 mV
Scan speed	2 mV s ⁻¹

[Measurement parameters begin]	
DP - Differential Pulse	
Initial purge time (s)	600
Conditioning cycles	
Start potential (V)	: 0.000
End potential (V)	: 0.000
No. of cycles	: 0
Hydrodynamic (measurement)	: No
Cleaning potential (V)	: 0.150
Cleaning time (s)	: 0.000
Deposition potential (V)	: -0.300
Deposition time (s)	: 60.000
Sweep	:
Equilibration time (s)	: 30.000
Start potential (V)	: -0.300
End potential (V)	: 0.1500
Voltage step (V)	: 0.001
Voltage step time (s)	: 0.400
Sweep rate (V/s)	: 0.002
Pulse amplitude (V)	: 0.050
Pulse time (s)	: 0.040
Cell off after measurement	: Yes
[Measurement parameters end]	

VR = 1-1 591

-0.29999	2.8656e-9
-0.29922	2.8473e-9
-0.29846	2.8717e-9
...	...
+0.14862	1.2265e-9
+0.14938	1.2506e-9
+0.15015	1.2885e-9

VR = 2-1 591

-0.29999	2.9786e-9
-0.29922	2.9847e-9
-0.29846	2.9664e-9
...	...
+0.14862	1.2265e-8
+0.14938	1.2506e-8
+0.15015	1.2885e-8

VR = 3-1 591

-0.29999	3.2166e-9
-0.29922	3.2136e-9
-0.29846	3.2258e-9
...	...
+0.14862	1.5045e-8
+0.14938	1.5500e-8
+0.15015	1.5836e-8

VR = 4-1 591

0.29999	3.1220e-9
-0.29922	3.1556e-9
-0.29846	3.1952e-9
...	...
+0.14862	1.6870e-8
+0.14938	1.7368e-8
+0.15015	1.7844e-8

-0.29999	2.8656e-9	2.9786e-9	3.2166e-9	3.1220e-9
-0.29922	2.8473e-9	2.9847e-9	3.2136e-9	3.1556e-9
-0.29846	2.8717e-9	2.9664e-9	3.2258e-9	3.1952e-9
...
+0.14862	1.2265e-9	1.2265e-8	1.5045e-8	1.6870e-8
+0.14938	1.2506e-9	1.2506e-8	1.5500e-8	1.7368e-8
+0.15015	1.2885e-9	1.2885e-8	1.5836e-8	1.7844e-8

Figure 3 Rearrangement of the data matrix obtained from the Voltammetric Analyzer.

These voltammograms were used to calculate the complexation capacity of copper (II) by the organic matter present in natural water and the conditional stability constant of the complex applying the method of Pardo et al. [12].

The file is opened in Origin as a set of data in ASCII format, the header contained in the file, sent by the potentiostat, is automatically eliminated in this step. Subsequently, the first column is marked, which contains the potential data referring to the range corresponding to the initial and final potentials, which are saved in memory.

Next, the first column (potentials) is eliminated, leaving only the column with current data from the various voltammograms. The file is converted into a matrix and the *Expand Columns* command is activated, informing the cutoff point in the single column of current values, relative to each voltammogram. Then the active matrix is transposed. The potential data, kept in memory, it is pasted into an empty column and this is the column with the abscissa (Figure 3). The number of columns (ordinate columns) will be the number of voltammograms plus the potential column (abscissa column). Then, all columns are marked, and a graph is made with all voltammograms.

The sequence of tasks performed in the Origin program facilitates the change of the alphanumeric data file to a numeric file, allowing viewing, from this numeric data file, all voltammograms (Figure 4a).

The voltammetric parameters are highlighted in blue, in green is the band of potential common to all voltammetric sweeps and in yellow are the current values for each voltammetric sweep.

The values of the complexation capacity and the conditional stability constant were determined using the titration curve, obtained from the construction of a graph of the maximum current values of the voltammograms versus the concentration of copper (II) added (figure 4b). This curve presented two straight lines with well-defined slopes. Determining the point of intersection of these two straight lines defined the complexation capacity value for each sample. The value of the conditional stability constant (K) was determined through the slopes of the two straight lines of the titration curve and the CC value, according to equation (3):

Equation (3) can be deduced according to:



$$K = \frac{[\text{CuL}]}{[\text{Cu(II)}]_{\text{free}} \cdot [\text{L}]}$$

$$[\text{CuL}] = [\text{Cu(II)}]_{\text{added}} - [\text{Cu(II)}]_{\text{free}}$$

$$[\text{Cu(II)}]_{\text{free}} = [\text{Cu(II)}]_{\text{added}} - [\text{CuL}]_{\text{complexed}}$$

$$K = \frac{[\text{Cu(II)}]_{\text{added}} - [\text{Cu(II)}]_{\text{free}}}{[\text{Cu(II)}]_{\text{free}} \cdot [\text{L}]}$$

As $\tan \alpha = m_a$ and $\tan \beta = m_b$, they can be expressed as:

$$m_b = \frac{i}{[\text{Cu(II)}]_{\text{free}}}$$

$$[\text{Cu(II)}]_{\text{free}} = \frac{i}{m_b}$$

$$m_a = \frac{i}{[\text{Cu(II)}]_{\text{added}}}$$

$$[\text{Cu(II)}]_{\text{added}} = \frac{i}{m_a}$$

$$\text{CC} = [\text{L}]$$

$$K = \frac{\frac{i}{m_a} - \frac{i}{m_b}}{\frac{i}{m_b} \cdot CC}$$

$$K = \frac{m_b - m_a}{m_a \cdot CC}$$

Figure 4a presents examples of voltammograms obtained for the determination of copper (II) in the total dissolved fraction of a sample of natural waters with the aim of determining the complexation capacity (CC) of dissolved organic matter in relation to copper (II) to evaluate the concentration of total ligands available and the conditional stability constant (K) of the complex formed.

From the voltammograms of this natural water sample, the titration curve was obtained by plotting graphs of the maximum current values as a function of the concentration of copper (II) added in the various microvolumetric additions.

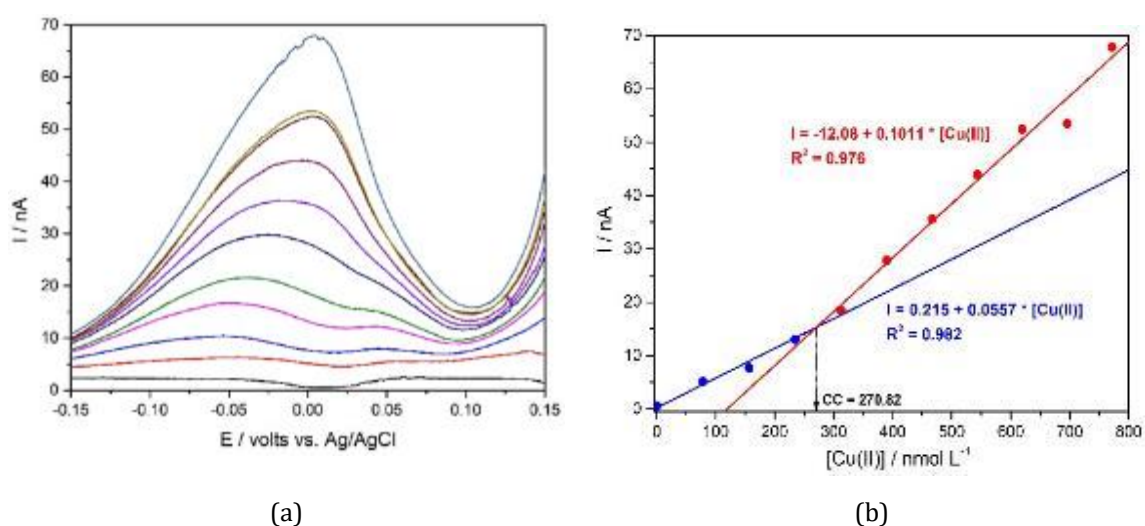


Figure 4 Voltammograms and titration curve for a natural water sample.

The graph presented two sets of points that were subjected to linear regressions, giving two straight lines with well-defined slopes (Figure 4b).

In the present case, the slopes of the lines are $m_a = 0.0557$ and $m_b = 0.1011$ and $CC = 270.82$, which gives a complexation constant equal to 3.01×10^{-6} or $pK = 6.48$.

4- Conclusion

The data obtained allowed us to conclude that the proposal of this experimental technique for determining the complexation constant, between humic substances present in natural waters and copper (II), is pertinent as a didactic experiment.

The use of the titration technique linked to voltammetry allowed the development of an experimental sequence favoring the determination of the complexation constant, and this is pertinent as it leads to an opening to develop the theory behind the voltammetric instrumentation used.

Compliance with ethical standards

Acknowledgments

The authors would like to thank the Minas Gerais State Research Support Foundation (FAPEMIG) for the financial support.

Disclosure of conflict of interest

No conflict of interest to be disclosed.

References

- [1] Van Elteren, J. T.; Urszula D.; Woroniecka, U. D. (2003). Investigation into sorption processes in the anodic stripping voltammetric speciation of Cu in natural waters. *Analytica Chimica Acta*, 476, 33–42.
- [2] Bryan, S. E.; Tipping, T.; Hamilton-Taylor, J. (2002). Comparison of measured and modelled copper binding by natural organic matter in freshwaters. *Comparative Biochemistry and Physiology Part C*, 133, 37–49.
- [3] Guibaud, G.; Tixier, N.; Bouju, A.; Baudu, M. (2004). Use of a polarographic method to determine copper, nickel and zinc constants of complexation by extracellular polymers extracted from activated sludge. *Process Biochemistry*, 39, 833–839.
- [4] Morrison, G. M. P.; Florence T. M. (1989). Comparison of physico-chemical speciation procedures with metal toxicity to *Chlorella Pyrenoidosa*. Copper complexation capacity. *Electroanalysis*, 1, 107-112.
- [5] Presa, M. J. R.; Catoggio, J. A.; Posadas, D.; Tucceri, R. I. (1997). Determination of the complexation capacity. Electrochemical lability in the absence of excess of ligand. *Journal of Electroanalytical Chemistry*, 432, 229-235.
- [6] Buffle, J. (1990). *Complexation reactions in aquatic systems: an analytical approach*. Chichester: Ellis Horwood Ltda.
- [7] Scarano, G.; Bramanti, E. (1993). Voltammetric behavior of marine hydrophobic copper complexes: effect of adsorption processes at a mercury electrode. *Anal Chim Acta*, 277, 137-144.
- [8] Pinheiro, J. P.; Mota, A. M.; Simões Gonçalves, M. L. (1994). Complexation study of humic acids with cadmium (II) and lead (II). *Analytica Chimica Acta*, 284, 525-537.
- [9] Custódio, G. (2001). Voltammetric determination of the complexation capacity of the waters of São Bartolomeu river. Master's Dissertation (Agrochemistry), Federal University of Viçosa, Brazil, 165 p.
- [10] Dutra, R. A.; Reis, E. L.; Reis, C.; Custódio, G.; Damasceno, O. I. C. (2021). Voltammetric determination of water complexation capacity of the Turvo Sujo river and of the São Bartolomeu stream sub-basins in Zona da Mata Mineira. *Journal of Engineering and Exact Sciences*, 7(2), 12172–01.
- [11] Microcal (2013). Origin 9.1, Microcal, Northampton, MA.
- [12] Pardo, R.; Barrado, E.; Vega, M.; Deban, L.; Tascón, M. L. (1994). Voltammetric complexation capacity of waters of the Pisuerga River. *Wat. Res.*, 28 (10): 2139-2146.