

## Potentiometric method for the determination of trace metal elements in water: the case of Cu (II), Fe (II) and Al (III)

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### Abstract:

The objective of this work is to develop a simple technique for the determination of trace metal elements, namely  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Al}^{3+}$  ions in an aqueous medium. To do this, regression lines correlating the potential difference (ddp) and the concentration of these ions were drawn using standard solutions prepared from standard solutions. The methodology consisted of using a multimeter equipped with two indicator electrodes (reference electrode and working electrode) and 2 cm distant. The results obtained show that the correlation coefficients  $r$  between the ddp read on the device and the concentrations of standard solutions of a single species or in the presence of other elements in solution vary between 0.99 and 1. This linearity was obtained to perform a comparative analysis of the measurement results with this method and the results of a DR3900. The proportional ratio of the two results obtained could confirm the possibility of determining the content of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Al}^{3+}$  ions by this technique in aqueous solution. The sensitivity of this method is 0.01mV/ppm. So for a variation of 1ppm, the ddp varies on average from  $10^{-5}\text{V}$ .

**Key Word:** Potentiometric; water; trace metal; ions; concentration.

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### I. Introduction

Heavy metals or trace metal elements are often present in very small quantities in environmental matrices [1, 2, 3]. They have a harmful and complex impact on living things and ecosystems. These impacts can be direct or indirect, acute or chronic [4]. The presence of these elements in the body can cause: irreversible neurobehavioral damage in many mammals and proximal tubules of the kidneys [5, 6, 7]. Based on the above, it is necessary and imperative to monitor the evolution of the content of these elements in the water. There are several techniques for detecting the presence of heavy metals in water and assessing their levels [8, 9]. These techniques are often complex, expensive and use chemicals that can pollute the environment. In addition, they require sampling and preservation of samples, which can influence the physicochemical parameters before analysis [10, 11, 12]. The objective of this study is to develop a simple, less expensive potentiometric assay technique to assay ions directly in water  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Al}^{3+}$  in situ to avoid variations in physicochemical parameters.

### II. Material And Methods

#### Materials

The experimental device used for the determination of heavy metals (Cu, Fe and Al) consists of a Silton 932 multimeter connected to two electrodes (one consisting of a plate of the element whose concentration of ions in solution is to be determined and another consisting of a plate of a metal whose standard torque potential ( $E^\circ$ ) is lower than the standard torque potential of the element to be measured). The electrodes (indicator and reference) are placed at a distance of 2 cm from each other. The plate of the element at the lower  $E^\circ$  constitutes the reference electrode. The reference electrode in the entire study is a lead (Pb) plate.

**Methods**

**Preparation of solutions**

The electrolytic solutions used in the various manipulations were prepared from standard 1000 ppm copper, iron and aluminium solutions kept cool. To account for interference, two types of solutions have been prepared. On the one hand, solutions from distilled water and the standard element alone in solution, and on the other hand, the element to be dosed in the presence of the other two elements taken from the standard solutions. The concentrations of the elements were varied.

**Determination of concentrations and establishment of calibration curves**

To determine the concentration of the different elements in solutions, 10 ml of the solution to be dosed was taken and introduced into a beaker. Then, the two electrodes (indicator and reference) are immersed in parallel in the analytical solution at the same depth and the ddp is read instantly on the multimeter. After each measurement, the electrodes are washed and rinsed with distilled water.

The curves were developed using the excel software.

**Table 1:** Composition of mixtures for the calibration of copper in solution

Mixing	Concentration of species present in ppm		
	Copper	Iron	Aluminium
Mix 1	0,5	3	1
Mix 2	1	0,5	3
Mix 3	3	1	0,5
Mix 4	5	0,5	1

**Table 2:** Composition of mixtures for the calibration of Iron in solution

Mixing	Concentration of species present in ppm		
	Iron	Copper	Aluminium
Mix 1	0,5	3	1
Mix 2	1	0,5	3
Mix 3	3	1	0,5
Mix 4	5	0,5	1

**Table 3:** Composition of mixtures for the calibration of Aluminium in solution

Mixing	Concentration of species present in ppm		
	Aluminium	Fer	Cuivre
Mix 1	0,5	3	1
Mix 2	1	0,5	3
Mix 3	3	1	0,5
Mix 4	5	0,5	1

**Comparative study**

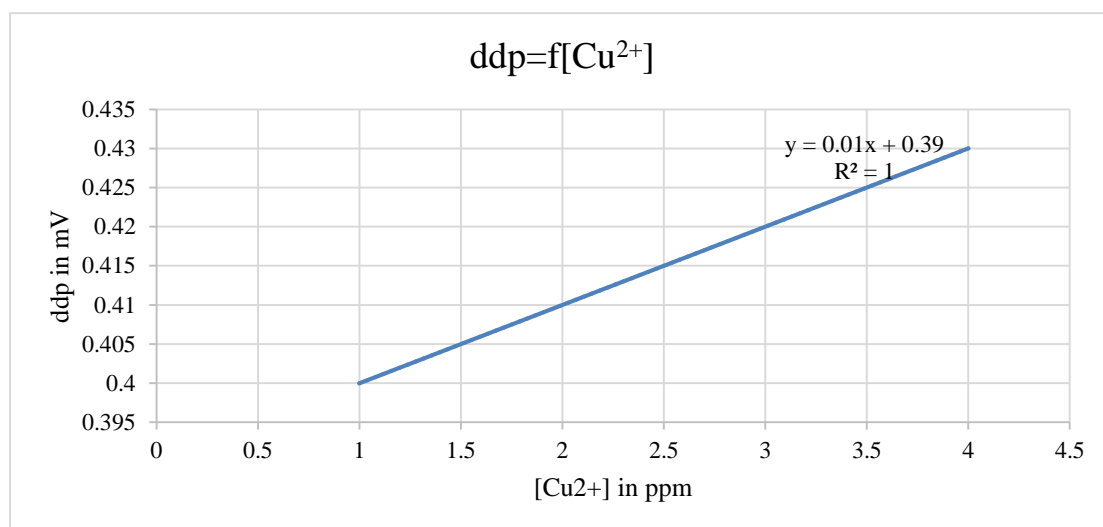
The Cu and Fe contents of three water samples from three different boreholes were determined on the one hand by the developed technique and on the other hand using a DR3900. The results were compared.

**III. Result And discussion**

**Calibration lines with a single species in solution**

**The case of copper(II) alone in solution**

Figure 1 below shows the result of the correlation between the concentration of copper(II) ions in solution and the potential difference read on the multimeter.

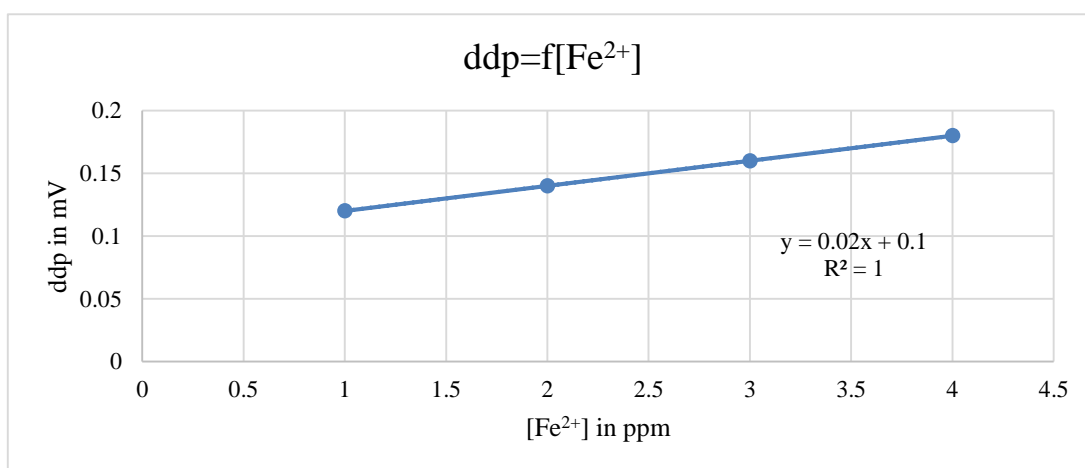


**Figure 1:** ddp regression curve as a function of copper(II) ion concentration

The regression curve in Figure 1 with  $r^2 = 1$  shows a very good correlation between the concentration of  $Cu^{2+}$  ions in solution and the ddp read. It indicates a proportionality between the concentration of  $Cu^{2+}$  ions in solution and the measured potential difference. This correlation shows that this technique can be used in the context of the determination of copper content in aqueous solution. The sensitivity obtained from the regression line is  $S=0.01$  mV/ppm.

#### The case of iron(II) alone in solution

Figure 2 below gives the result of the correlation curve between the concentration of  $Fe^{2+}$  ions in the solution and the potential difference read on the multimeter.

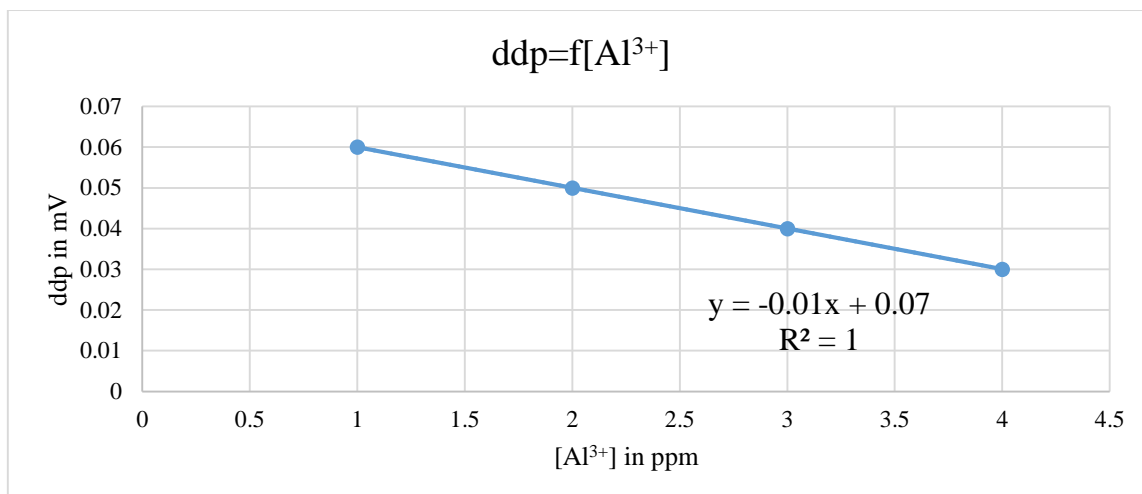


**Figure 2:** Regression curve of ddp as a function of iron(II) ion concentration

The calibration curve shown in Figure 2 with  $r^2 = 1$  also shows a very good correlation between the concentration of iron(II) ions in solution and the ddp read. It indicates a proportionality between the concentration of  $Fe^{2+}$  ions in solution and the measured potential difference. This result also confirms the reliability of this method in the determination of  $Fe^{2+}$  ion content in aqueous solution. The sensitivity obtained from the regression line is  $S=0.02$  mV/ppm.

#### Case of aluminium (III) alone in solution

Figure 3 shows the result of the correlation curve between the concentration of the aluminium ions and the ddp read on the multimeter.



**Figure 3:** Regression curve of ddp as a function of Al<sup>3+</sup> ion concentration

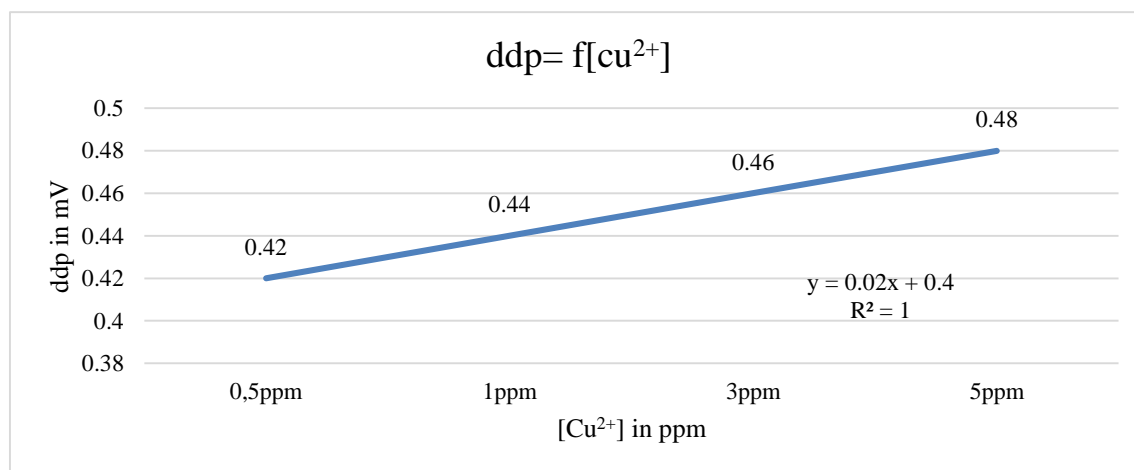
Curve 3 with  $r^2 = 1$  and  $S = -0.01$  mV/ppm, also shows a very good correlation between the concentration of aluminum ions in solution and the ddp read. It indicates a proportionality between the concentration of Al<sup>3+</sup> ions in solution and the measured potential difference. This result also confirms the reliability of this method in the determination of the aluminium ion content in aqueous solution. The sensitivity obtained from the regression line is  $S = -0.01$  mV/ppm.

For Al, there is a decrease in the regression curve.

**Regression line with the three species (Cu, Fe and Al) in solution**

**The case of the determination of copper (II) in the presence of Fe and Al in solution**

Figure 4 shows the results of the ddp measured as a function of the concentration of copper ions in an electrolyte also containing Fe<sup>2+</sup> and Al<sup>3+</sup> ions in different proportions.

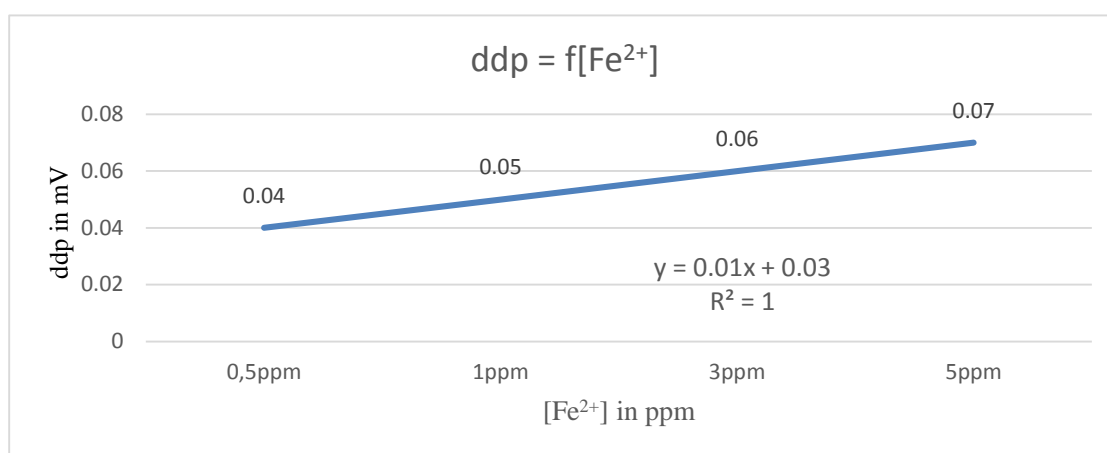


**Figure 4:** Regression curve of ddp measured as a function of Cu concentration

The calibration line shown in Figure 4 with  $r^2 = 1$  shows a very good correlation between the concentration of Cu<sup>2+</sup> ions in solution and the ddp read. It indicates a very good proportionality between the concentration of copper (II) ions in solution and the difference in measured potential. The correlation coefficient  $r^2 = 1$  in both cases (the element alone in solution or in the presence of the other two elements). This result indicates that the presence of the other two elements has no influence on the proportionality between the concentration of the element in solution and the read ddp. On the other hand, there has been a doubling of the influence on sensitivity. The sensitivity obtained from the regression line is  $S = 0.02$  mV/ppm.

**The case of the determination of iron (II) in the presence of Cu(II) and Al (III) in solution.**

Figure 5 shows the values of the measured ddp as a function of the concentration of Fe<sup>2+</sup> ions in an electrolyte also containing Cu<sup>2+</sup> and Al<sup>3+</sup> ions in different proportions.

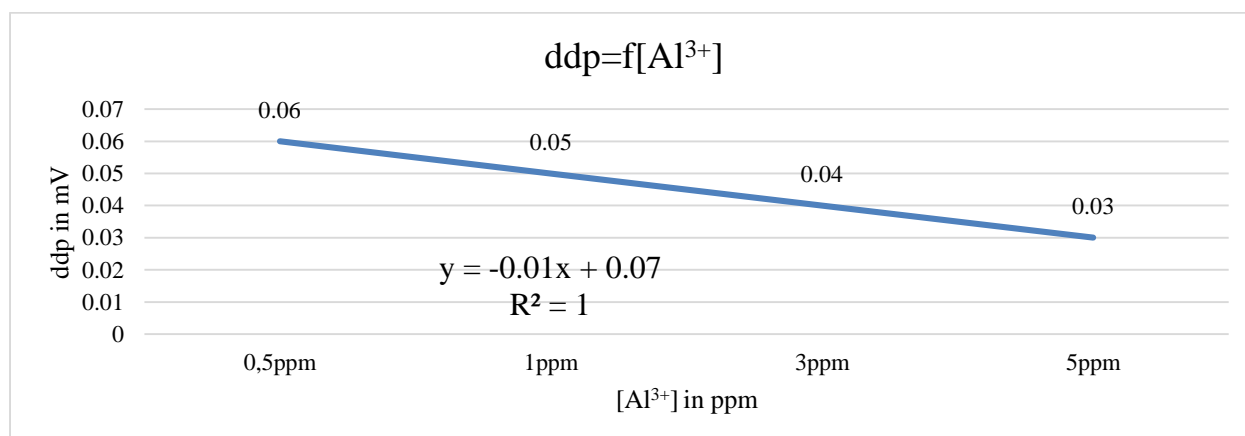


**Figure 5:** Regression curve of the ddp measured as a function of Fe<sup>2+</sup> concentration in the presence of Cu<sup>2+</sup> and Al<sup>3+</sup>.

The calibration line shown in Figure 5 with  $r^2 = 1$  shows a strong correlation between the concentration of iron(II) ions in solution and the ddp read. It shows a good proportionality between the concentration of iron (II) ions in solution and the difference in potential read. The correlation coefficient  $r^2 = 1$  in both cases (the element alone in solution or in the presence of the other two elements). This result shows that the presence of the other two elements has no influence on the proportionality between the concentration of the element in solution and the read ddp. The sensitivity obtained from the regression line is  $S=0.01$  mV/ppm, identical to that obtained with the element alone in solution.

#### Case of the determination of Al<sup>3+</sup> ions in the presence of Cu<sup>2+</sup> and Fe<sup>2+</sup> ions solution

Figure 6 shown below shows the values of the measured ddp as a function of the concentration of Al<sup>3+</sup> ions in an electrolyte containing the Cu<sup>2+</sup> and Fe<sup>2+</sup> ions.



**Figure 6:** Regression curve of the ddp measured as a function of the concentration of Al<sup>3+</sup> ions in the presence of Fe<sup>2+</sup> and Cu<sup>2+</sup> ions

The calibration line shown in Figure 6 with  $r^2 = 1$  shows a very good correlation between the concentration of Al (III) ions in solution and the ddp read. It indicates a very good proportionality between the concentration of Al (III) ions in solution and the measured potential difference. The correlation coefficient  $r^2 = 1$  in both cases (the element alone in solution or in the presence of the other two elements). This result indicates that the presence of the other two elements has no influence on the proportionality between the concentration of the element in solution and the read ddp. The sensitivity obtained from the regression line is  $S=-0.01$  mV/ppm, identical to that obtained with the element alone in solution.

### Comparative study

#### The case of the determination of iron or Cu in solution

Tables IV and V below give respectively the  $Fe^{2+}$  and  $Cu^{2+}$  ion contents of three different borehole water samples ( $E_{483}$ ,  $E_{481}$ , and  $E_{Sounci}$ ) and ( $E_{512}$ ,  $E_{521}$ , and  $E_{516}$ ) obtained on the one hand by the developed technique and on the other hand by a DR3900. R1 represents the results obtained from the developed technique and R2 represents those obtained from DR3900 for the  $Fe^{2+}$  ion content. The  $\frac{R2}{R1}$  ratio is the coefficient of proportionality between R2 and R1 for each sample ( $E_{483}$ ,  $E_{481}$ , and  $E_{Sounci}$ ). R3 represents the results obtained from the developed technique and R4 represents those obtained from DR3900 for the  $Cu^{2+}$  ion content. The  $\frac{R4}{R3}$  ratio is the coefficient of proportionality between R3 and R4 for each sample ( $E_{512}$ ,  $E_{521}$ , and  $E_{516}$ ).

**Table 4:**  $Fe^{2+}$  ion contents obtained from a DR3900 and the technique developed

Echantillons	$E_{483}$	$E_{481}$	E (sonusi)
Result			
Measurement result obtained = R1	12 ppm	9ppm	8ppm
Result of DR3900 = R2	0,32 ppm	0,18ppm	0,18ppm
$\frac{R_2}{R_1}$	0,02	0,02	0,02

**Table 5:**  $Cu^{2+}$  ion contents obtained from a DR3900 and the technique developed

Echantillons	$E_{512}$	$E_{521}$	$E_{516}$
Result			
Measurement result obtained = R3	151,54 ppm	86,47ppm	137,16ppm
Result of DR3900 = R4	0,085 ppm	0,048ppm	0,076ppm
$\frac{R_4}{R_3}$	$5,56.10^{-4}$	$5,55.10^{-4}$	$5,55.10^{-4}$

Tables 4 and 5 show different results for each sample. The results obtained from the developed technique are superior to those obtained with the DR3900. On the other hand, for each species measured ( $Fe^{2+}$  or  $Cu^{2+}$ ), the concentration ratio is the same for all samples. This report indicates that the method developed in this work can be used for the determination of  $Fe^{2+}$  or  $Cu^{2+}$  ions in water. This difference in results (technique developed and that of DR399) requires further investigations to know whether sampling and sample storage actually influence the analysis results.

### IV. Conclusion

The objective of this work is to develop a potentiometric technique for the determination of trace metal elements, namely the ions in aqueous solution  $Cu^{2+}$ ,  $Fe^{2+}$  and  $Al^{3+}$  ions. The correlation coefficients obtained between the measured ddp and the concentrations of  $Cu^{2+}$ ,  $Fe^{2+}$  and  $Al^{3+}$  ions show that this developed potentiometric assay method can be used for the determination of these elements in waters. Also, the results obtained show that the presence of ions of the two elements other than the element to be measured in the reaction media does not influence the determination of the ion considered. The sensitivity of the method for Cu or Al alone or in the presence of others is the same. On the other hand, for iron, in the presence of other elements, the sensitivity varies. Comparative analysis with the DR3900 indicates the possibility of determining Fe, Cu and Al by the developed method. The method developed shows the need for investigation into the possibility of influence of sampling and sample conservation on the analysis results.

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