



# Spectrophotometric determination of zinc and copper in a multi-syringe flow injection analysis system using a liquid waveguide capillary cell: Application to natural waters

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## ABSTRACT

This work exploits a multi-syringe injection analysis (MSFIA) system coupled with a long liquid waveguide capillary cell for the spectrophotometric determination of zinc and copper in waters. A liquid waveguide capillary cell (1.0 m pathlength, 550  $\mu\text{m}$  i.d. and 250  $\mu\text{L}$  internal volume) was used to enhance the sensitivity of the detection. The determination for both ions is based on a colorimetric reaction with zincon at different pH values. The developed methodology compares favourably with other previously described procedures, as it allows to reach low detection limits for both cations (LODs of 0.1 and 2  $\mu\text{g L}^{-1}$ , for copper and zinc, respectively), without the need for any pre-concentration step. The system also provided a linear response up to 100  $\mu\text{g L}^{-1}$  with a high throughput (43  $\text{h}^{-1}$ ) and low reagent consumption and effluent production. The developed work was applied to natural waters and three certified reference water samples.

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## 1. Introduction

In recent years, due to the increase of pollution strictly connected with human activity, quantitative routine analysis has been in focus. Flow analysis systems, especially in water analysis, are very suitable for this purpose because of increased accuracy, good reproducibility, precision, equipment cost, elevated throughput, simplified sample handling, reduced contamination risks, high degree of automation and reduction in the consumption of samples/reagents and in effluent production [1,2]. Within the various flow methods, one of the most recent is MSFIA. It was first proposed by Cerdà et al. [3] and along with other flow analysis techniques, it presents versatility, robustness, high sample throughput and low consumption of reagents and samples [4]. MSFIA combines the multi-channel operation of flow injection analysis with the ability to select the required volume of sample and reagents for analysis, a characteristic feature of sequential analysis (programmable flow) mode. Therefore, MSFIA can be an advantageous alternative to downscale environmental monitoring assays.

Zinc and copper ions are essential for normal physiological processes of living organisms [5]. In humans, zinc is the second most abundant transition metal ion, acting in several biological systems and is also a cofactor in diverse biochemical processes of bacte-

ria and plants [6]. It is an essential nanonutrient in ocean surface waters and can be present in organically complexed and in phytoplankton integrated forms [7]. Copper also plays an important role as a component of some oxidoreductases in the growth of phytoplankton [8] as well as in most living organisms [9]. Excessive amounts or defects in intake of both ions cause several possible alterations to physiological processes [5,10]. In humans, the maximum daily intake of 0.5 and 1.0  $\text{mg kg}^{-1}$  was established, for copper and zinc, respectively [11]. Excessive amounts of zinc found in the environment can have diverse origins: domestic, metallurgy galvanising, alloy manufacturing, agricultural, clinical, geological, pharmaceutical products [12,13] and copper is often connected to effluents from septic tanks and municipal wastewaters, discharges from power plants as well as leaching from antifouling paints and pressure-treated docks pilings [14–16]. Moreover, both ions are often found together in many samples of distinct nature [17,18] and this reason justify the development of a low cost method able to determine both ions at low levels.

There are several methods for the determination of both analytes or just a single one. Within the methods used for the determination of both analytes in waters, the majority are based on spectrophotometry [10,11,17–22], but voltammetric detection was also employed by Shams et al. [11] and Suteerapataranon et al. [23]; this technique can have limitations in the zinc determination due to hydrogen wave interference in acidified samples along with the incapacity to detect Zn at natural pH (near 8) at which Zn is strongly connected to organic ligands [7]. There are also several ICP

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The spectrophotometric measurements were carried out at the wavelength of 620 nm.

As detection system, an Ocean Optics PC2000-ISA (Dunedin, FL, USA) spectrophotometer, a pair of 200  $\mu\text{m}$  fiber optic cable, a DH-2000 deuterium halogen light source (Top Sensor Systems, Eerbeek, The Netherlands) and a liquid waveguide capillary cell (LWCC 2100, World Precision Instruments, Sarasota, USA) (1.0 m pathlength, 250  $\mu\text{L}$  inner volume, 550  $\mu\text{m}$  inner diameter) was used.

Data acquisition was performed by Auto-analysis computer software.

### 2.3. MSFIA configuration and procedure

The MSFIA system (Fig. 1) was designed to allow the determination of copper and zinc in waters at low levels. In order to attain this objective, a LWCC was coupled to the MSFIA manifold. Four solenoid valves were included in the set-up. The sample introduction from one of the syringes by impulsion would require cumbersome washing steps of the syringe itself to avoid contamination between consecutive solutions. For that reason, additional solenoid valves (V5, V6) were attached to the system to accommodate the aspiration based sampling. The volume of the sample introduced was controlled by the length of the sample loop placed between V5 and V6. Confluence ( $c_2$ ) was added to promote mixing between the sample and the buffer solution. The solenoid valve V7 was used for the introduction of the sample or standard solution and V8 for the selection of the buffer solutions.

The protocol sequence is listed in Table 1. The first step consists of aspirating 1.0 mL of the sample/standard and respective buffer solution to the sample loop. Afterwards, the mixture contained in the sample loop (SL) was propelled with the carrier to the confluence ( $c_1$ ) where a portion of the colour reagent (0.25 mL) was introduced downstream. In the final step, the resulting mixture was transported to the detector.

The calculation of the analytes concentrations was based on the following procedure. Calibrations curves were traced at pH values of 5 and 9. At pH 5, copper standards in the range 10–100  $\mu\text{g L}^{-1}$  were introduced in the flow system and the copper sample concentration was estimated by interpolation. Then, at pH 9 (equivalent sensitivity for copper and zinc), a calibration curve was established with zinc standards in the same working range and, by interpolation, the sum of the molar concentrations of both ions was obtained. Therefore, the zinc sample concentration can be assessed by the difference.

At the end of a working day, the LWCC was washed consecutively with HCl (0.05  $\text{mol L}^{-1}$ ) and NaOH (0.05  $\text{mol L}^{-1}$ ) solutions in counter current.

## 3. Results and discussion

### 3.1. Study of physical and chemical parameters

Several physical parameters such as flow rate, sample and reagent plug volumes along with chemical parameters, for instance reagent concentrations, were studied in order to optimise the system. The univariate method was used, where only one parameter was changed while others kept constant.

Initial studies were carried out to optimise the physical parameters for the zinc determination since the objective was to use the same system (manifold) for both determinations and this assay has lower sensitivity. Previous experiments with LWCC equipment allowed to conclude that its applicability is limited by the blank absorbance values of the solutions [37]. For this reason, this study was focused on increasing sensitivity while maintaining low blank absorbance values. The sample loop (SL) volume was varied within

250–650  $\mu\text{L}$ . It was noticed that sensitivity and the blank values were higher with the increase of the volume. A good compromise between the sensitivity and the blank values was achieved at 400  $\mu\text{L}$ . The effect of reaction coil length was studied over the range of 50–200 cm. The sensitivity increased through the range studied, although between 125 and 200 cm, the blank signal stabilised; therefore, 200 cm was selected. The influence of the reagent plug size was also studied between 125 and 500  $\mu\text{L}$ . This study was carried out by changing the time interval that the valve 3 was kept open. Under these conditions, the volume of 250  $\mu\text{L}$  was chosen, since for higher volumes the sample dilution effect became more considerable and sensitivity did not increase any further.

The monitoring wavelength was varied within 615–625 nm and 620 nm allowed the best sensitivity. An attempt to reduce blank values was made by subtracting the absorbance values registered of several wavelengths between 650 and 800 nm in order to reach lower detection limits. None of them improved sensitivity; therefore no absorbance subtraction was carried out.

With regard to the first analytical step, the aspiration of sample/standard with respective buffer solution, it should be stated that a larger portion (1 mL) than the capacity of SL (400  $\mu\text{L}$ ) has to be aspirated in order to promote a better mixture. Mixing was assumed to be satisfactory if repeatability of the signals yielded RSD values lower than 5%. The effect of the aspiration flow rate for the first step (Table 1) was tested in the range of 1–15  $\text{mL min}^{-1}$ , and 5  $\text{mL min}^{-1}$  presented good mixing. The flow rate in the second and third step of the analytical cycle was varied between 1.5–4.5 and 2–5  $\text{mL min}^{-1}$ , obtaining the best sensitivity at 2.25 and 4  $\text{mL min}^{-1}$ , respectively.

The influence of chemical variables was also studied in order to improve the system performance. Firstly, the reagent concentration was tested over the range of  $4.625 \times 10^{-7}$  to  $4.625 \times 10^{-4} \text{ mol L}^{-1}$  and the best sensitivity was obtained with a  $4.625 \times 10^{-5} \text{ mol L}^{-1}$ .

The concentration and the pH of the borate buffer were also studied for the zinc determination. The concentration was studied within 0.04–0.5  $\text{mol L}^{-1}$  and 0.25  $\text{mol L}^{-1}$  was chosen, since for higher levels, the sensitivity remained constant. In literature, different pH values were referred for the zinc determination. This colorimetric reaction can be carried out at pH values between 8 and 10. In the present study the best sensitivity was obtained at pH 9.0. A batch study was performed by mixing the same sample/buffer proportions (1:1) in a scaled up volume, in order to prove that the concentration chosen was high enough to ensure a final sample solution pH around 9.0 units.

Regarding the chemical variables for the copper determination, only the concentration of the buffer solution needed to be tested. Thus, the effect of the concentration of sodium acetate solution was studied within 0.05–0.5  $\text{mol L}^{-1}$ . The best sensitivity was obtained for a concentration of 0.25  $\text{mol L}^{-1}$ . At higher concentrations the sensitivity of the system kept constant. The pH of this buffer solution was set to 5.0 units to minimise the formation of the Zn–zincon complex.

### 3.2. Interference studies

Several possible interference ions were tested in the determination of zinc or copper. Deviations higher than  $\pm 5\%$  of the absorbance level of the respective standard (20  $\mu\text{g L}^{-1}$ ) were considered as interference. The ions studied in this experiment were  $\text{Fe}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Mn}^{2+}$  at concentrations of 20, 40, 200, 1000, 2000 and 20,000  $\mu\text{g L}^{-1}$ , respectively (Table 2). Sodium citrate is referred in the literature as a masking agent used in buffer streams with the aim of avoiding interferences from iron, aluminium and manganese [18]. Therefore, the use of sodium citrate was tested: it was incorporated in the buffer solution for the zinc determination and the interference of several ions was significantly reduced although the

**Table 1**  
MSFIA protocol sequence for the determination of zinc and copper in waters.

Step	Piston movement	Position of solenoid valves							Volume (mL)	Flow rate (mL min <sup>-1</sup> )	Action
		V1	V2	V3	V5	V6	V7	V8			
1	Pick up	0	1	0	1	1	1	1 <sup>a</sup> /0 <sup>b</sup>	1.0	5	Aspirate sample and buffer solution
2	Dispense	1	0	1	0	0	0	0	0.5 C 0.25 R	1.5 C 0.75 R	Propel carrier and colour reagent to the detector
3	Dispense	1	0	0	0	0	0	0	2.0	4	Propel the mixture to the detector and signal registration

C, carrier; R, colour reagent; 0, off; 1, on.

<sup>a</sup> Copper buffer solution.

<sup>b</sup> Zinc buffer solution.

**Table 2**  
Study of interfering species expressed as relative deviation from the absorbance value obtained for the standard solution of 20 µg L<sup>-1</sup> of copper or zinc.

Species tested	Copper concentration (µg L <sup>-1</sup> )	Difference (%)	Zinc concentration (µg L <sup>-1</sup> )	Difference (%)
Iron	40	+5.3	200	+3.6
Aluminium	2000	−4.9	200	+4.9
Cadmium	20,000	+4.8	40	+5.1
Manganese	200	+4.8	20	+3.3
Lead	20,000	+5.1	1000	+5.4

sensitivity dropped a lot. Therefore, it is not an efficient solution to reach low concentration levels and so the use of sodium citrate was discarded. For copper determination, the major interference was from iron at a level two times higher followed by manganese at a level ten times higher. The iron interference can be masked by the addition of ferrozine. Manganese levels in fresh, river and seawater samples are lower than the tolerated concentration for copper determination [38]. For zinc determination, manganese interferes at the same level of concentration and cadmium at a level two times higher. Aluminium and iron interfere at a level hundred times higher. Copper determination was less susceptible to interference from the species tested than the zinc determination.

### 3.3. Figures of merit

The overall features achieved for both determinations are summarised in Table 3. The limit of detection (LOD) and limit of quantification (LOQ) were calculated as the concentration corresponding to three and ten times the standard deviation of the blank, respectively [39]. The linear ranges obtained for both species were similar.

**Table 3**  
Figures of merit of the developed method.

Parameters	Values	
	Zinc	Copper
Detection limit (µg L <sup>-1</sup> )	2	0.1
Quantification limit (µg L <sup>-1</sup> )	4	0.8
Working range (µg L <sup>-1</sup> )	Up to 100	Up to 100
Determination rate (h <sup>-1</sup> )	43	43
Reagent consumption per assay (µmol)		
Zincon	0.01	0.01
Sodium acetate	–	140
Boric acid	18	–
Potassium chloride	7	–
Sodium hydroxide	35	–
Waste produced per assay (mL)	3.75	3.75

### 3.4. Application to water samples

The developed system was applied to the determination of zinc and copper in different types of water samples in order to assess its accuracy.

Firstly, recovery tests were prepared using both species in different types of water samples: surface (sea), ground (well and spring) waters. Table 4 summarises the results obtained at three levels of additions (4, 10 and 20 µg L<sup>-1</sup>) for both species. The recovery results obtained are very acceptable although for zinc determination the standard deviations are higher than for copper. During the experiments using the proposed method some differences were noticed between the behaviour of the two species. For example, in the zinc calibration curves the absorbance signal obtained for consecutive injections of concentrations higher than 50 µg L<sup>-1</sup>, was constantly increasing, and when the blank solution was injected once more, the absorbance signal was higher compared to the initial injection. However, after cleaning the LWCC with HCl solution 0.5 mol L<sup>-1</sup> the blank signal was reduced to the initial value. This effect could be explained by the formation of precipitates in the solutions and their accumulation at the LWCC walls. We must keep in mind that the buffer solution used for zinc determination has pH 9.0 and the internal diameter of LWCC has 0.6 mm. At this reaction pH, in natural water samples, solubility problems may occur due to metallic hydroxide species and the repeatability of the analytical signal can be deteriorated [18]. Before analysing certified reference water samples, studies were carried out on the reaction response to the presence of both analytes. As above mentioned, at pH 9.0 zincon reacts with both analytes, therefore a comparison study using equal molar concentrations of zinc standards and copper with zinc standards (mixed standards) was performed. The equation obtained with zinc standards and with zinc and copper standards (mixed standards) is  $Abs_{620\text{ nm}} = 0.502 (\pm 0.063) C_{Zn} + 0.272 (\pm 0.052)$  and

**Table 4**  
Results obtained for recovery tests with zinc and copper in different types of water.

Analyte	Sample number	Recovery (%) <sup>a</sup>		
		Concentration added		
		4 µg L <sup>-1</sup>	10 µg L <sup>-1</sup>	20 µg L <sup>-1</sup>
Zinc	1	102 ± 6	96 ± 4	103 ± 6
	2	96 ± 6	93 ± 2	104 ± 6
	3	94 ± 7	107 ± 9	104 ± 3
	4	104 ± 4	107 ± 5	105 ± 1
Copper	1	97 ± 2	100 ± 2	102 ± 1
	2	102 ± 1	102 ± 1	103 ± 1
	3	102 ± 3	99 ± 1	104 ± 1
	4	99 ± 5	95 ± 3	94 ± 1

1, well water; 2, spring water; 3, groundwater; 4, seawater.

<sup>a</sup> Mean and standard deviation of 5 replicates.



**Table 5**

Results obtained for the determination of copper and zinc in three certified reference water samples.

Sample	Copper ( $\mu\text{g L}^{-1}$ )		Zinc ( $\mu\text{g L}^{-1}$ )	
	MSFIA-LWCC	Certified value <sup>d</sup>	MSFIA-LWCC	Certified value <sup>d</sup>
ERM-CA021a	2028 $\pm$ 50 <sup>a</sup>	1975 $\pm$ 54	669 $\pm$ 231 <sup>a</sup>	514 $\pm$ 9
NIST-SRM 1640	87 $\pm$ 2 <sup>b</sup>	85.2 $\pm$ 1.2	67 $\pm$ 6 <sup>b</sup>	53.2 $\pm$ 1.1
NWRI-TM-24.2	8.2 $\pm$ 0.2 <sup>c</sup>	7.3 $\pm$ 0.1	22.8 $\pm$ 2.8 <sup>c</sup>	20 $\pm$ 0.5

<sup>a</sup> Standard deviation ( $n = 20$ ), dilution 50 times.

<sup>b</sup> Standard deviation ( $n = 10$ ), dilution 5 times.

<sup>c</sup> Standard deviation ( $n = 10$ ), no dilution.

<sup>d</sup> Mean and associated uncertainty.

$\text{Abs}_{620\text{nm}} = 0.471 (\pm 0.049) C_{\text{ZnCu}} + 0.286 (\pm 0.041)$ , respectively. The equation values obtained for the two standard curves show no significant difference, indicating additive behaviour. At pH 9.0 when separated standard solutions of zinc and copper are analysed equivalent sensitivities were obtained. When zinc standard solutions were analysed at pH 5.0 the absorbance values obtained for all the standards are equal to blank absorbance value, demonstrating that there is no reaction between zinc and zincon at this pH.

Therefore, when the two analytes are simultaneously present in the sample, Cu(II) concentrations can be assessed directly from calibrations performed at pH 5.0, while the quantification of zinc has to be based on the already defined copper concentration and on the calibration curve established for Zn at pH 9.0.

The developed system was applied in the quantification of Zn and Cu in three certified reference water samples: NWRI-TM-24.2, NIST-SRM 1640 and ERM-CA021a. The results obtained are summarised in Table 5. Two out of the three reference materials analysed had certified concentration values higher than the upper limit of application range, therefore dilution of these samples was needed. From the results obtained several conclusions can be pointed out. First, the quality of the results (RSDs) obtained for copper determination is better than the ones obtained for zinc determination and it should be reminded that the errors in the determination of zinc are affected by the deviations obtained in copper determination. Second, the copper determination does not seem to be affected by the different degrees of dilution while in the zinc determination the standard deviations obtained are increasing with the dilution.

#### 4. Conclusions

The proposed work provides a good alternative for the spectrophotometric sequential determination of copper and zinc at low levels in a simple and low cost way with elevated throughput and low reagent consumption (green chemistry approach). Comparing to other previous flow methods displaying similar working ranges, the manifold is simpler as it was not necessary to use a pre-concentration step to reach such low levels of both metals. The present strategy is the first one in the literature to use the LWCC detection cell for the determination of the two analytes and underlines the usefulness of this detection cell for the simultaneous determination, even at this low concentration levels.

The developed work compared well with other spectrophotometric flow methods using the same reagent as can be concluded from Table 6 (in electronic supplementary information). It presents several advantages as low detection limits achieved without a pre-concentration unit, low reagent consumption, high sampling rate and it was successfully applied to different water types. Analytical characteristics of other applications, using different detection

modes, like voltammetry [11,23]; molecular spectrophotometry [12,16,22,40–42,44–46] atomic absorption spectrophotometry [5,34], fluorimetry [6,7] and chemiluminometry [43] are presented in a form of a table (Table 7) within the electronic supplementary information. The table allows us to conclude that in those environmental samples where trace levels of these metals have to be assessed only luminometric assays [6,7,43] give a comparable alternative (in terms of potential portability and detection limits) to the one presented here.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2011.01.023

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