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Chemofiltration of eriochrome black T-zinc complex and determination by X-ray spectrometry

Mabel Vega^a, Miriam Augusto^a, María C. Talío^b, Liliana P. Fernández^{b,*}^a Instituto de Ciencias Básicas, FFHA, Universidad Nacional de San Juan, Av Libertador San Martín 1109-Oeste, 5400 San Juan, Argentina^b Área de Química Analítica, Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, Instituto de Química de San Luis (INQUISAL-CONICET), Chacabuco y Pedernera, 5700 San Luis, Argentina

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ABSTRACT

In the present work, a new methodology for zinc preconcentration and separation and its determination by X-ray spectrometry is proposed. The methodology is based on the formation of a complex using Eriochrome black T (1-naphthalensulfonic acid, 3-hidroxy-4-((1-hidroxy-2-naphtalenyl)azo)-7-nitro, monosodium salt), EBT, as complexing agent. Next, the complex is retained on a polyamide membrane by a chemofiltration process. The chemofiltrated material on the membrane constitutes a thin film, which minimizes or eliminates the interelemental effects when the instrumental detection is realized by X-ray fluorescence spectrometry. As the preconcentration method presented is based on the formation of a complex which will interact with the membrane during the chemofiltration, it was necessary first to establish the optimal conditions for the complex formation of Zn-EBT in aqueous medium and then to explore the optimal conditions for obtaining the thin film. The pH dependence of the metal ion chemofiltration on the membrane and other variables, such as contact time and retention capacity of the membrane, were also optimized. Chemofiltration step provided an enrichment factor of 30,000, improving considerably the instrumental detection limit, allowing the determination of trace zinc in environmental samples.

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1. Introduction

The determination of heavy metals in natural waters is a task for analytical chemists frequently asked by environmentalist, for the evaluation and phenomenon interpretation of aquatic systems. However, in many cases the available analytical instrumentation does not show enough sensibility for the realization of the analysis in these natural samples. As such, a previous preconcentration step results necessary, and it is for this reason many enrichment procedures have been proposed.

Zinc is an essential trace element of great importance for humans, plants, and animals. It plays an important role in several biochemical processes, and its compounds have bactericidal activity [1]. Zinc compounds have been used in solutions as antiseptic and disinfectant agents. However, if it is in excess, this metal can produce some damage in the human body, including disturbances in energy metabolism or increasing oxidative stress [2]. Therefore, sensitive, selective, and rapid methods for determination of zinc are in great demand [3]. Spectrophotometry [4,5], atomic absorption spectrometry [6,7], neutron activation analysis [8], inductively coupled plasma-atomic emission spectroscopy [9,10], and inductively coupled plasma-mass spectrometry

[11,12] are widely applied to the determination for zinc at trace levels.

The determination of zinc in residual water samples is one of the most difficult and complicated analytical tasks, especially at trace levels. In trace analysis, preliminary analytical procedures, such as preconcentration or selective separation of the analyte prior to its determination, are frequently necessary in order to minimize or eliminate the interferences caused by the matrix.

During the last years a great number of preconcentration and separation techniques have been reported. However, the need for rapid and selective methods of preconcentration has led to the development of new methodologies. They involve preconcentration methods like precipitation [13,14], ion exchange [15], immobilizing reagents [16], chelating resins [17–19], between others.

The method here suggested is based to a certain extent upon the earlier developed principle of element concentration by coprecipitation with organic reagents from diluted solutions. This procedure cannot provide high concentration coefficients. These drawbacks can be overcome by membrane chemofiltration. X-ray fluorescence (XRF) analysis is a versatile method of analysis that continues to be the subject of many research investigations, widely used for the analysis of the major and trace elements, where the highest degree of precision and accuracy is required [20].

The main principle of the preconcentration method here presented is the formation of a complex of zinc with a selective organic reagent,

* Corresponding author.

E-mail address: lfernand@unsl.edu.ar (L.P. Fernández).

sodium 3-hydroxy-4-((1-hydroxy-2-naphthalenyl)azo)-7-nitro-1-naphthalensulfonate (EBT), in solution. The following step is a filtration of the system during which the formed complex is retained leading to the formation of a thin film of the deposited solid on the membrane. This fact allows high selectivity and the interelemental effects produced by the matrix spectrometry can be eliminated in XRF determination [21].

2. Experimental

2.1. Reagents

Standard solutions of Zn(II) (1000 mg/L) were prepared by dissolving 1.0661 g of $\text{Zn}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$ (Hopkin & Williams Ltd., Chadwell Heath, Essex, England) in 0.1 mol/L HCl and diluting to 250 mL with doubly distilled water.

EBT ($\text{C}_{10}\text{H}_{12}\text{N}_3\text{NaO}_7\text{S}$) was purchased from Merck (Darmstadt, Germany), 95% purity. A $1 \cdot 10^{-3}$ mol/L solution of EBT was prepared by dissolving 410 mg of the reagent in doubly distilled water up to 100 mL.

Working standard solutions were prepared by diluting with doubly distilled water adequate volumes of concentrated solutions.

Buffer solutions of pH 4 and pH 10 were prepared with 5×10^{-2} mol/L potassium biphthalate (Merck, Darmstadt, Germany) and 1×10^{-2} mol/L sodium tetraborate (Mallinckrodt Chemical Works, New York, Los Angeles, St. Louis, USA), respectively, for calibrating the pH-meter electrode.

All other chemicals used were of analytical grade, and doubly distilled water was used throughout.

Membrane polyamide filter papers (Millipore, Sao Paulo, Brazil) of 0.45 μm pore size were used in chemofiltration processes.

2.2. Apparatus

A PhilipsPW1400 X-ray Fluorescence Spectrometer was used for Zn K_{α} line measurement. The measurement parameters were $2\theta = 41.520$. Rh tube, 50 kV, 50 mA, LiF(200) crystal, 75–25% window width, counting time for peak and background 50 s, and a gas proportional-scintillation counter in tandem arrangement was used for the analysis.

A Mayer 4001 UV-Visible Spectrometer with glass cells of 10 mm path length was used in spectroscopic studies of EBT-Zn(II) complex.

The pH of the solutions was measured by a 211-Microprocessor pHmeter (HANNA Instruments, USA).

The filtrations were performed in special filtration equipment with a vacuum pump.

2.3. Studies of the Zn(II)-EBT complex formation

2.3.1. Influence of pH

Solutions containing $4 \cdot 10^{-6}$ mol/L Zn(II) and $4 \cdot 10^{-5}$ mol/L EBT were adjusted to different pH values with 0.01 mol/L NaOH (Mallinckrodt Chemical Works, NY, Los Angeles, St. Louis, USA) or 0.01 mol/L HCl (Merck, Darmstadt, Germany). Absorbance was measured at 545 nm against reagent blank.

2.3.2. Zn(II)/EBT ratio

Solutions containing different Zn(II)/EBT ratios were adjusted at pH 10.4 with 0.01 mol/L NaOH. The complex concentration was determined spectrophotometrically at 545 nm.

2.4. Studies of chemofiltration process

2.4.1. Effect of pH

Portions of 25 mL of solution containing the complex Zn(II)/EBT (1:5) were adjusted to different pH values with HCl or NaOH. The

solutions were filtered through polyamide membrane and the K_{α} lines of the analyte were measured by XRF spectrometry. All intensities measured were corrected for background intensity.

2.4.2. Capacity of retention of the membrane

Solutions containing different concentrations of the complex Zn(II)/EBT at pH 9.5 were filtered through the membrane to determine the maximum retention capacity. Zinc K_{α} line was measured in the chemofiltrate on the membrane by XRF.

2.4.3. Determination of the critic thickness

Systems were prepared at pH 9.5 using maximum quantity of EBT allowed by the polyamide membrane and increasing Zn(II) concentration. Solutions were filtrated and they were measured by XRF using Zinc K_{α} line.

2.4.4. Determination of Zn in presence of Ca (II) and Mg (II)

Solutions containing the complex Zn(II)/EBT at pH 9.5 and different concentrations of Ca (II) and Mg (II), were passed through the membrane. The metal K_{α} line was measured in the chemofiltrate on the membrane by XRF.

2.4.5. Determination of Zn(II) in natural water samples

A series of appropriate standard solutions of Zn(II) and a sample of natural water from Guanacache Lake were preconcentrated by chemofiltration through a polyamide membrane and their Zinc K_{α} line X-ray fluorescence lines were measured.

3. Results and discussion

3.1. Zn(II)-EBT complex formation equilibrium by absorption spectrometry

Aqueous solution of Zn(II)-EBT complex exhibits a maximal absorbance at 545 nm. The highest absorbance was obtained at pH 10.4. Thus, the subsequent experiments were carried out at this pH value.

It was also necessary to establish the optimum metallic ion/chelant ratio. This was determined by continuous variations method establishing a 4:1 EBT:Zn(II) ratio (Fig. 1). In order to assure quantitative Zn(II) complexation, in subsequent assays, an excess of 10:1 EBT:Zn(II) was used.

3.2. XRF study of Zn(II)-EBT chemofiltration

The retention of Zn(II)-EBT complex on the polyamide membrane from the aqueous solutions at various pH values was examined using batch procedure. The retention was quantitative between pH values of 8.5 and 10. The results of the influence of pH on the chemofiltration of Zn(II)-EBT are shown in Fig. 2. A pH value of 9.5 was selected as optimal for following assay.

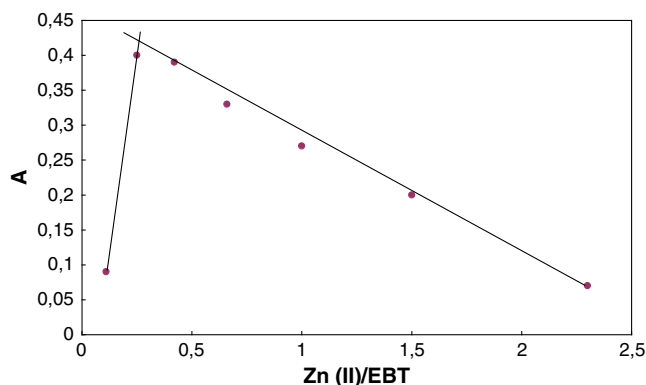


Fig. 1. Determination Zn (II)/EBT stoichiometry by continuous variation method using molecular absorptiometry. pH 10.4; $\lambda = 545$ nm.

This behavior can be explained taking into account that polymeric membrane at basic pH values is present in cationic form. Savvin et al. [22,23] suggest that the retention mechanism of the metal ions and the organic reagent complex on the polyamide membrane filter is based not only on electrostatic forces but also on non-hydrophobic interactions between the polymeric matrix and the molecules of organic reagent.

The influence of the shaking time on the chemofiltration process was studied varying this parameter from 5 to 30 min for systems prepared with Zn(II) and EBT solutions. A shaking time of 5 min resulted enough for reaching the complex retention maximum.

Obtained results permit to establish that neither the complex formation reaction nor its interaction with the membrane constitutes velocity controlling steps in the kinetic of preconcentration process. Consequently, these steps enable to a reasonable whole time of analysis.

The saturation study permitted to establish a maximum concentration of EBT of $3.8 \cdot 10^{-4} \text{ mol.L}^{-1}$. Above this concentration, membrane holes were saturated by excess of EBT.

Considering the complex stoichiometry previously determined (4:1) and the maximum EBT concentration admitted by the membrane in the chemofiltration process, systems were preparing varying Zn(II) concentrations and filtrated through the membrane. Zn K_{α} line was measured by XRF. In Fig. 3 the plot shows the XRF intensity as a function of Zn amount retained on the membrane. For very low Zn concentrations, the XRF intensity is proportional to concentration. The plot is linear up to $6 \cdot 10^{-5} \text{ mol L}^{-1}$ of Zn(II). The intensity deviates from linearity for higher Zn(II) complex concentration values, due to the saturation of the membrane.

Working below this concentration it can be sure that the membrane is not saturated and the complex retained constitutes a thin film. The calculate critical thickness was determined at $7.65 \cdot 10^{-5} \text{ mol.L}^{-1}$ of Zn(II).

The importance of measuring the analyte on a thin film lies in that the intensity of the analyte is proportional to its concentration, and absorption-enhancement effects produced in XRF are negligible. Neither primary nor analyte X-ray lines are significantly absorbed in the thin layer. This fact allows high selectivity and interelemental effects produced by the matrix in XRF can be eliminated.

The enrichment factor [24] defined as:

$$F = (Q_T/Q_M)/(Q_T^0/Q_M^0)$$

where Q_T^0 and Q_T are the analyte quantity before and after of preconcentration process, and Q_M^0 and Q_M are the amounts of the matrix before and after of enrichment.

Considering a film thickness of $4 \mu\text{m}$ and an area of 1.767 cm^2 on the surface of the polyamide membrane obtained by chemofiltration

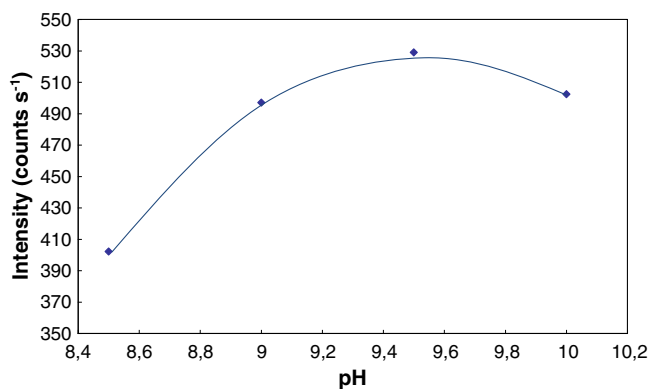


Fig. 2. Influence of pH on the chemofiltration of Zn(II)-EBT complex. Zn K_{α} line; [Zn(II)] = $4 \cdot 10^{-6} \text{ mol L}^{-1}$; [EBT] = $4 \cdot 10^{-5} \text{ mol L}^{-1}$.

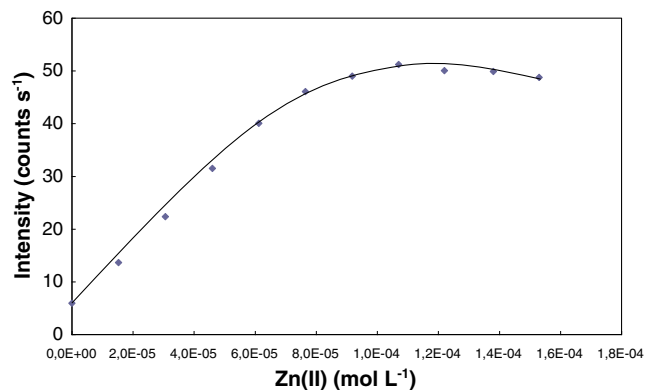


Fig. 3. Saturation curve for chemofiltration of Zn(II)/EBT complex. Zn K_{α} line; [EBT] = $4 \cdot 10^{-5} \text{ mol L}^{-1}$; pH = 9.5.

of 25 mL of 5 mg.L^{-1} Zn(II), an enrichment factor of 30,000 was obtained.

3.3. Analytical parameters

Table 1 summarizes the studied experimental variables, the optimal values for preconcentration of Zn(II) on membranes and analytical parameters. The limit of detection (LOD) was calculated as 3 s/m , where s is the standard deviation of 10 successive means of the blank and m is the slope of the calibration curve (calibration sensitivity). The limit of quantification (LOQ) was calculated as 10 s/m . Range of linearity was evaluated by checking the linear regression coefficient (r^2) of the calibration curve. The linearity of the calibration curve was considered acceptable when $r^2 > 0.998$.

3.4. Interferences

Experiences have proved that XRF interferences are eliminated when it is working in thin film conditions [25]. This fact result of great importance since neither primary nor analyte X-ray lines are significantly absorbed in the thin layer, so absorption-enhancement effects are negligible. The thin film preparation realizes the determination without interferences since each atom in the film absorbs and emits independently from the others.

Previous data of water proceeding of Guanacache Lake have showed elevated levels of Ca (II) and Mg (II). These cations form complexes with EBT. This situation could be unfavorable for Zn(II)-EBT complex formation. This fact did necessary to explore the effect of potential interferences on Zn(II) XRF determination.

Assays were realized by adding increasing amounts of Ca(II) ($0\text{--}20 \text{ mg L}^{-1}$) on Zn(II)-EBT systems and filtering on membranes. XRF signal of Zn(II) K_{α} line presented an enhancement of approximately 40%, when the interfering was present in a concentration of 20 mg L^{-1} .

In the case of Mg(II) assays, the enhancement was significantly superior, causing an increase of 300% on zinc RXF signal, for interfering levels of 20 mg L^{-1} .

Table 1 Studied optimal experimental conditions and analytical parameters for Zn(II) determination.

Parameters	Studied range	Optimal conditions
pH of chemofiltration	8.5–10.5	9.5
Buffer sodium tetraborate	$1 \cdot 10^{-3}$ – $4 \cdot 10^{-2} \text{ mol/L}$	$1 \times 10^{-2} \text{ mol/L}$
EBT concentration	$4 \cdot 10^{-5}$ – $4 \cdot 10^{-3} \text{ mol L}^{-1}$	$4 \cdot 10^{-5} \text{ mol L}^{-1}$
LOD	–	0.06 mg L^{-1}
LOQ	–	0.21 mg L^{-1}
LOL	–	$0.21\text{--}100 \text{ mg L}^{-1}$

Table 2
Recovery study. Zn(II) determination in natural water of Guanacache Lake (San Juan, Argentine).

Sample	Zn(II) added (mg L ⁻¹)	Zn(II) found ± SD (mg L ⁻¹)	Recovery (%; n = 6)
1	–	1.33 ± 0.02	–
	2.00	2.42 ± 0.16	104.60
	6.00	7.35 ± 0.11	100.40
2	–	0.41 ± 0.02	–
	1.00	1.36 ± 0.10	95.00
	1.50	1.88 ± 0.01	98.00
3	–	0.61 ± 0.06	–
	1.00	1.62 ± 0.05	101.00
	1.50	2.07 ± 0.15	97.33
4	–	1.68 ± 0.08	–
	0.50	2.16 ± 0.02	96.00
	1.50	3.26 ± 0.05	105.33
5	–	1.09 ± 0.21	–
	4.00	4.87 ± 0.24	94.50
	6.00	6.72 ± 0.30	93.83

This fact does the indispensable application of standard addition method for Zn(II) determination by XRF in water samples with elevated Ca(II) and Mg(II) levels.

3.5. Validation and applications

The accuracy of the methodology was performed using the standard addition method. The reproducibility was evaluated repeating the proposed approach 6 times for each sample. The recoveries of Zn(II) in five samples beginning Guanacache Lake (San Juan, Argentine), based on the average of replicate measurements, are illustrated in Table 2; the obtained results showed that the proposed method is suitable for determination of Zn(II) in such samples, for all range of studied concentrations.

4. Conclusions

Zinc is an essential trace element of great importance for humans, plants, and animals. However, if it is in excess, it can produce alteration in energy metabolism or increasing oxidative stress. The developed methodology represents a promising approach in the area of environmental monitoring. This work presents the study of complex formation between Zn(II) and EBT as a previous step to the development of a preconcentration method for Zn(II) by chemofiltration. Thin film preparation allows suppressing the matrix interferences (interelemental effects) for Zn(II) determination by X-ray fluorescence spectrometry. The high enrichment factor obtained (30,000 fold) for the proposed preconcentration method encouraged to propose this methodology as a worthy tool in Zn(II) trace analysis.

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