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TECHNICAL NOTE

Evaluation of Sisal Fiber as Biosorbent for online Preconcentration and Determination of Cu and Mn coupled to MP AES using the Analytical Greenness Metric Approach

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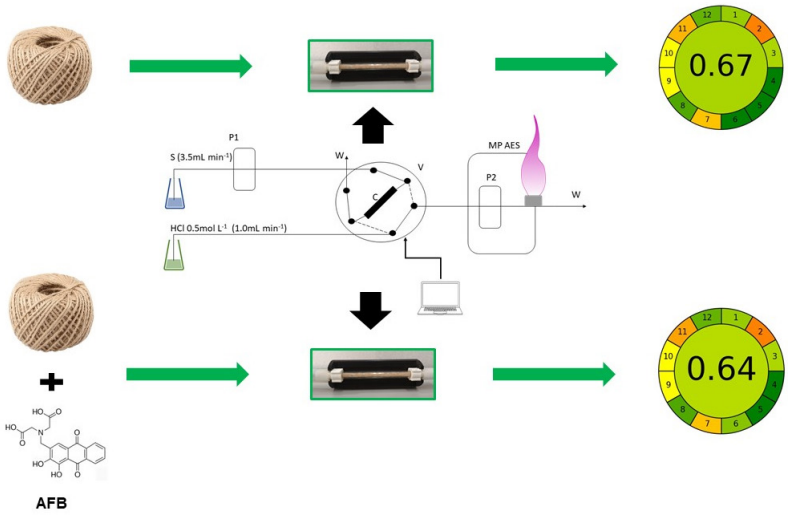

Biorsorbents can be used to pack minicolumns for the preconcentration of trace elements and thus improve the detection limits of some techniques. A biosorbent is efficient when presents binding sites as carbonyls, amines, and carboxylic groups, among others. Thus, natural materials as the sisal fiber (*Agave sisalana*) may be a good candidate. Sisal fiber demonstrated good performance for Cu preconcentration when it was impregnated with alizarine fluorine blue (AFB). However, very good results were reported for the first time by our group with this column, without the use of additional reagents for both, Mn and Cu determinations in water samples by using microwave plasma atomic emission spectroscopy (MP AES). In this paper a comparison of the sisal fiber preparation with and without impregnation with AFB is presented and discussed in terms of the figures of merit, including precision, trueness, limits of detection and quantification. In addition to that, the number of determinations without the need of replacement of the solid phase was evaluated. Results demonstrated that the impregnation of sisal fiber with AFB does not leads to an improvement in the analytical performance.
Analytical Greenness Metric Approach (AGREE) was used to evaluate the greenness of both methods and results obtained were similar. Despite this, the method without impregnation of the fiber has some remarkable advantages, that contributes to Green Analytical Chemistry (GAC), related to the lifetime of the sorbent, not considered in the AGREE tool.

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INTRODUCTION

Sorption is a physico-chemical process through which a substance binds to another, resulting in an accumulation or preconcentration of the sorbate in the sorbent. When the solid sorbent is the surface of a biological matrix, the process is called biosorption. Different biosorbents have good affinity for sorbates when they have a large number of binding sites such as carbonyls, carboxylic groups, and amines, among others. Compared with commercial sorbents, usually used, biosorbents are less expensive, and are renewable materials, even agro-industrial residues can be used for these purposes. All these characteristics are in good agreement with the principles of Green Analytical Chemistry (GAC).[1-5]

Cellulose, lignocellulose which are present in the cell wall of plant material has hydroxyl and carboxylic groups, which are responsible for the use of materials such as sisal fiber, sorghum, among other plant materials. These materials can be used for remedial purposed and some applications in Analytical Chemistry.[6-10] In addition, plant-based biosorbents stand out due to the simple pre-treatment needed prior to their use for analytical purposes.[3]

Several applications were reported using sisal fiber (*Agave sisalana*) for metal preconcentration; all of them impregnate the sisal fiber with different reagents.[9,11] One of the most used is the sisal fiber derivatized with alizarine fluorine blue (AFB).[9] However, in a previous work, we found very good results using the sisal fiber packed in a minicolumn without the use of additional reagents for the determination of manganese (Mn) and copper (Cu) in waters and subsequent simultaneous determination by microwave plasma atomic emission spectroscopy (FI-MP AES).[12]

Considering how important it is nowadays to develop greener and simpler analytical methods, a comparison was made between the performances of the method using sisal fiber without AFB derivatization and derivatized. For this purpose, Analytical Greenness Metric Approach (AGREE) was applied, this tool was selected because it shows through pictograms how greener and simpler a method is and it is easy to interpret.[13,14] However, this tool have some limitations that were discussed.

Results showed that the use of sisal fiber without adding any external reagent was successfully applied for online preconcentration of Cu and Mn in waters.

MATERIALS AND METHODS

Reagents

Manganese and cooper standards were prepared using a 1000 mg L^{-1} commercial solution (TraceCERT, Switzerland) by suitable dilutions with ultrapure water. Ultrapure water (18.2 MΩ.cm) was obtained from a purification equipment (DirectQ3 UV, Millipore, Darmstadt, Germany). A 0.01% (w/v) alizarine fluorine blue (AFB) solution was prepared by dissolving the solid (98%) (Sigma Aldrich, St Louis, MO, USA) in ultrapure water. Other reagents were of analytical grade. The glassware was kept overnight in a nitric acid solution (10% (v/v)) and after that rinsed with ultrapure water.

FI-MP AES system

A flow injection (FI) manifold with the capability of online preconcentration was coupled to a MP AES for simultaneous determination of Mn and Cu. A minicolumn was placed in a 6-port valve packed with sisal fiber for the preconcentration of both analytes in water samples prior the determination by MP AES. Figure 1 represents the flow injection system. A 6-port injection valve with a microelectronic actuator-controlled module (two-position, Valco Cheminert Instrument VICI, Co Inc., CoH, USA) was employed. Liquids were propelled by a peristaltic pump (Rainin Dynamax RP-1, USA) with Tygon™ tubing. The valve was controlled by a personal computer (RS232 serial port). The injection valve control and the preconcentration and elution stages were performed automatically by a program written in Python ™. The operation of the flow injection system consists of the preconcentration of sample for 90 s. Then the valve (V) commute and the eluent drags the analyte towards detection system. Connections were of Teflon™ PFA tubing (id 0.8 mm).[12]

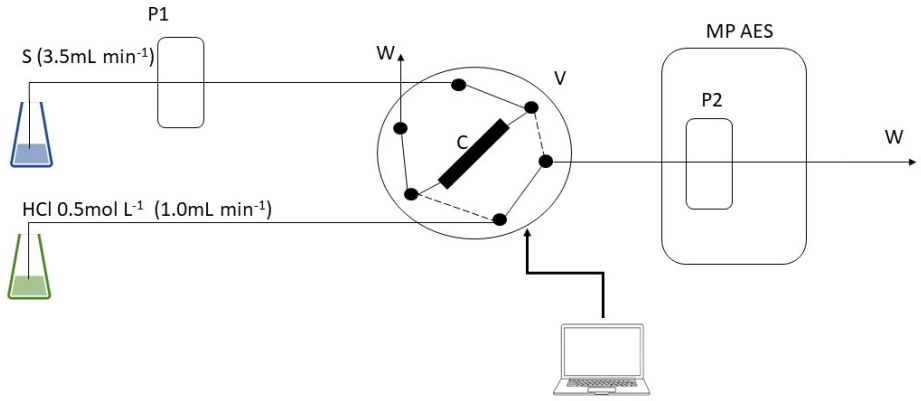

Figure 1. FI system coupled to MP AES. **P1 and P2:** peristaltic pumps; **V:** injection valve; **W:** waste; **S:** standard or samples; **C:** minicolumn; **HCl:** hydrochloric acid (eluent); solid lines represent position during the preconcentration step and dotted lines represent the valve position during the elution.

Minicolumn

A minicolumn was designed using a glass tube of 2.2 mm internal diameter and 5 cm long and packed with 100 mg of the sisal fiber.[12] The sisal fiber was purchased in a local market (sisal thread) and was treated with HNO_3 (10% v/v), washed with ultrapure water, and dried in an oven at 60 °C during 12 h, as it was reported by the authors dos Santos et al.[8] For comparison purposes the experiments were run using the biosorbent without derivatization and also with the sisal fiber impregnated with Alizarine Fluorine Blue (AFB) according to what was reported by de Souza Días et al.[9] Briefly, the functionalization consisted of passing through the minicolumn (containing 100 mg of Sisal fiber) a 0.01% (w/v) AFB solution at a flow rate of 10 mL min^{-1} during 10 minutes. After that a washing step with 1.0 mol L^{-1} NaOH and 1.0 mol L^{-1} HNO_3 solutions were carried out and finally rinsed with ultrapure water.

Instrument

The analytical determinations were performed using a MP AES spectrometer (MP AES, Agilent 4210, Santa Clara, CA, USA) equipped with a standard torch and a glass cyclonic spray chamber and a One Neb Serie2 nebulizer. Nitrogen was generated with an Agilent 4107 Nitrogen generator (Agilent, Santa Clara, CA, USA), using an air compressor (Dürr Technik, Bietigheim-Bissingen, Germany). Analytical signals were obtained using the analytical lines were 403.08 nm for Mn and 324.75 nm for Cu in Time Scan mode, and data exported as csv format were then processed through the software Peak Simple™ (SRI, CA, USA).

Instrumental parameters and operating conditions are shown in Table I. Operating conditions such as nebulizer flow and viewing position were optimized with a solution containing 2 mg L^{-1} of both analytes.

Table I. Instrument parameters and operating conditions

Instrument parameter	
Microwave frequency (MHz)	2450
Applied plasma power (Kw)	1.0
Stabilization time (s)	0
Background correction	Auto
Reading time (s)	1
Sample introduction system	
Nebulizer flow (L min^{-1})	0.9
Viewing position	10 (Cu); -10 (Mn)

Optimization

The influence of the variables: preconcentration time and pH was evaluated in previous work for the system without AFB.[12] Considering the optimum parameters obtained before; the critical variables were also investigated for the method with sisal-AFB.

Method validation

The analytical procedure validation was performed following the recommendations of Eurachem Guide.[15] The evaluated figures of merit for both methods were precision, linearity, limit of detection (LOD), limit of quantification (LOQ), and trueness.

RESULTS AND DISCUSSION

Optimization

The use of sisal fiber impregnated with AFB was reported by de Souza Dias et al, for the preconcentration of Cu but not for Mn.[9] Herein, the developed FI-MP AES system was evaluated for the simultaneous determination of Mn and Cu. To study the influence of critical variables, two experiments were carried out using a 0.2 mg L^{-1} standard solution of Cu and Mn and preconcentration time and pH were evaluated. Figures 2 and 3 present experimental conditions and results.

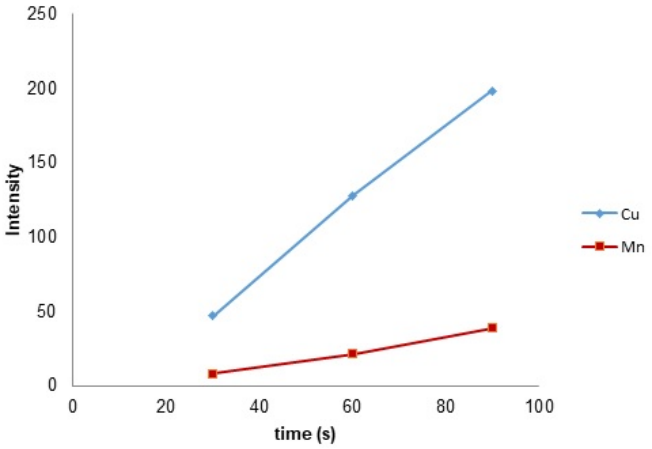

Figure 2. Effect of the preconcentration time.

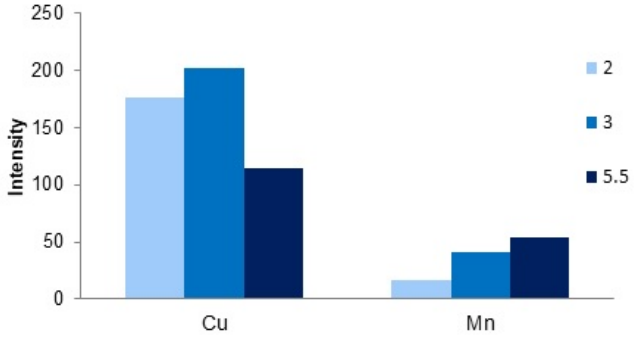

Figure 3. Effect of the pH in the preconcentration step.

For subsequent tests, a preconcentration time of 90 seconds and pH equal to 5.5 were selected as optimum conditions.

Method validation

Validation of the online preconcentration of Mn and Cu using sisal fiber impregnated with AFB and subsequent simultaneous determination by MP AES was carried out following the guidelines of the Eurachem Guide.[15] Linearity was evaluated by visual inspection and the coefficient of determination (R^2) from the calibration curves. The determination coefficients obtained for the linear regressions were greater than 0.99 for both elements. Detection (LOD) and quantification (LOQ) limits were estimated as the analyte concentration corresponding to 3 and 10 times the standard deviation of a Cu and Mn standard solution of 0.05 mg L^{-1}. Spiked samples were analysed for the evaluation of the trueness. Well water samples were spiked at a level of 0.1 mg L^{-1} for Mn and Cu respectively and a recovery (%R) assay was performed. Precision was expressed as the relative standard deviation (n=6, RSD %).

In a previous work we reported the preconcentration and simultaneous determination of Mn and Cu (FI-MP AES) with a minicolumn packed with sisal fiber without impregnation.[12] Table II summarized the figures of merit of both FI-MP AES methods. The preconcentration of Mn using standard solutions with the sisal fiber impregnated with AFB was satisfactory to evaluate linearity and to estimate the RSD, LOD and LOQ. However, in the recovery test of the spiked well water samples, the results were not adequate. No antecedents about preconcentration of Mn with sisal-AFB where found. No further studies were done since the aim of this note is to present the advantages of a simple method without impregnation with AFB.

Table II. Performance comparison

	Cu		Mn	
	sisal fiber[12]	**sisal fiber with AFB**	**sisal fiber[12]**	**sisal fiber with AFB**
Linearity (µg L^{-1})	12 – 500	12-500*	30 – 500	33-500*
LOD (µg L^{-1})	3.7	3.8	9.0	9.8
LOQ (µg L^{-1})	12	12	30	33
Trueness (%R)**	97	77	98	27
RSD % ***	4.3	2.1	2.6	3.1
Number of determinations without replacement of the packing	350	40	350	40
Sampling frequency (sample per hour)	20			

*Studied range; **average, n=6; ***spiked samples (n=6); limit of detection (LOD); limit of quantification (LOQ).

When comparing the figures of merit, it was observed that the impregnation of the sisal fiber with AFB does not lead to an improvement in the analytical performance. This demonstrates that the use of the sisal fiber without the need of impregnation with an additional reagent is a suitable possibility for the online preconcentration of Cu and additionally Mn can be determined simultaneously by FI-MP AES.

Green Analytical Chemistry Evaluation

To evaluate de greenness of both FI-MP AES methods developed, the analytical greenness metric approach (AGREE) was used.[13] AGREE is a metric tool that evaluates the 12 principles of the GAC (SIGNIFICANCE) on a scale (0 – 1). As a result of this, a pictogram is generated indicating a final score of the method. This score is shown in the center of the pictogram thus indicating the greenness of the method, if this value is close to 1 then the color is dark green being the method greener.

Results of application of the AGREE tool to the developed methods are shown in Figure 4. Both methods are similar in terms of greenness as can be seen in the corresponding pictograms. However, the method without impregnation of the fiber is simpler as it does not require an additional reagent. It also presents as advantages the possibility of performing simultaneous determination of Mn and Cu, and also as a remarkable difference in the number of determinations without the need of replacing the packing, 350 *vs* 40 determinations. Both advantages, not shown using the AGREE tool contributes to GAC. This kind of tools are very simple to use, but sometimes incomplete, this lead the researchers to have a critical point of view about new methods that includes a cost-benefit evaluation.

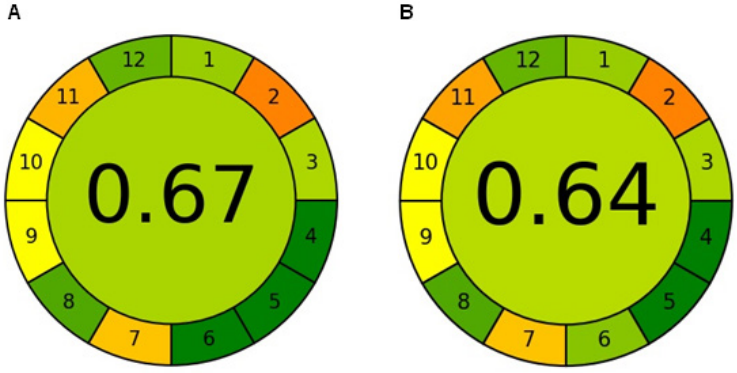

Figure 4. Results of AGREE analysis: (A) fiber without impregnation, (B) fiber impregnated with AFB.

CONCLUSIONS

A FI system coupled to MP AES was validated for the online preconcentration of Mn and Cu using a biosorbent. Considering the antecedents of impregnation of the sisal fiber with AFB, a comparison of the figures of merit of both methods was performed concluding that impregnating the sisal fiber with AFB does not lead to an improvement. The use of sisal fiber without the need to impregnate with a reagent turned out to be an efficient and very cheap biosorbent with up to 350 determinations, not requiring a replacement of the packing.

Applying the AGRRE tool, the greenness of both methods was evaluated. Based on the results of the study, both methods are aligned with the main principles of the GAC. Nevertheless, the use of the sisal fiber without any additional reagent showed to be more efficient which conducts to use these systematized “green” tools with a critical view.

Conflicts of interest

Authors declare no conflict of interest.

Acknowledgments

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