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Chitosan-modified cotton thread for the preconcentration and colorimetric trace determination of Co(II)

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ABSTRACT

In this work we propose a thread-based microfluidic device (μTAD) for the preconcentration and colorimetric determination of Co(II) in water using a digital image. The reaction is based on complexation of Co(II) by 4-(2-pyridylazo) resorcinol (PAR), which changes the detection zone from yellow to red. PAR is immobilized in a chitosan membrane to retain the complex in the detection zone. The designed μTAD makes it possible to preconcentrate and determine cobalt between 25 and 600 $\mu g \cdot L^{-1}$ with a relative standard deviation of 4% ($n = 5$), and a detection limit of 6.5 $\mu g \cdot L^{-1}$. The device permits an enhancement factor of 11 by combining the use of a chitosan retention membrane and a sample volume of 50 μL. Recovery experiments were performed in tap water to evaluate the accuracy of the method, and the results obtained compared to a reference method presents an error no higher than 5.7%.

1. Introduction

As an effect of anthropogenic activity, the disposal of industrial waste is the main source of river contamination with heavy metals. Some production processes are responsible for the contamination of waterways with elements. In addition to industrial activities, the incineration of urban waste also produces metal-rich fumes, mainly mercury, lead and cadmium. The metals resulting from these processes can be solubilized by water, damaging the health of humans and animals, given the toxic potential of these elements [1]. Contact with these substances can cause serious health problems, such as nervous system dysfunction and cancer. In addition, the toxic action of metals may lead to the death of species or bioaccumulation, which potentiates the harmful effect of substances through food chains, also endangering the lives of animals that are not directly involved in the problem. Moreover, when deposited into the ocean, these elements can permanently contaminate the aquatic fauna and flora [2]. Among the metals that cause water pollution, cobalt is particularly notable. An organic form of cobalt is essential in the body because it is a component of cyanocobalamin (vitamin B12). However, inorganic species of cobalt are toxic, causing nausea, vomiting and even serious heart problems [3]. In light of the foregoing, it is necessary to determine the content of heavy metals in water to order to take the appropriate action.

In this context, microfluidic devices have greatly impacted analytical chemistry research with their potential application in the determination of metals in water due to their exceptional characteristics, such as sample introduction and pretreatment, chemical reaction, analytical separation and identification in a single device [4]. Several devices have been developed for the quantification of heavy metals in waters. Particularly interesting are the ones constructed with paper, which are known as μPAD (Microfluidic Paper-based Analytical Device) [5–14].

Nevertheless, paper as a support has a disadvantage as it requires patterning to define the device channels. In order to overcome that deficiency, a new type of substrate has been increasingly used: thread. Called μTAD (Microfluidic Thread-based Analytical Device), this substrate has drawn the attention of the scientific community because of its ideal characteristics, such as low-cost material, flexible and resistant filament structure, a high specific surface area that reduces reaction time, possible three-dimensional structure formation, analytical operations on the device, small sample volumes and reagents, a low detection limit, and results obtained with smartphone applications [15–21].

Moreover, the use of thread not only permits the transport of

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aqueous and non-aqueous fluids by hydrophilic multifilament via capillary action, but also has properties for building fluid transport pathways in microfluidic devices, because they can be sewn onto various support materials without the need for the patterned hydrophobic barriers essential for paper-based microfluidic devices. The thread can be used to manufacture fabrics capable of reaching the hydrophilic-hydrophobic contrast desirable for creating hydrophilic channels to control fluid flow [22].

In general, colorimetric reactions are the most commonly used for the quantification of heavy metals, but one of the disadvantages is the frequent presence of species of interest in complex matrices and/or in concentrations below the limit of detection, which makes determination impossible. It is possible to bypass this difficulty by using separation and/or preconcentration procedures. These procedures involve different analytical techniques, such as liquid–liquid extraction, coprecipitation and solid-phase extraction (SPE). The SPE process takes advantage of the ability of certain solids to concentrate the species present in solutions on their surface. For an efficient adsorption process, it is necessary to consider a high adsorption capacity for the removal of the adsorbate. In addition, the adsorbent must be available in large quantities and be low in cost [23–25].

Coloured digital images like those obtained from the μTAD can be represented by different colour spaces, such as RGB (Red, Green and Blue) or HSV (Hue, Saturation, Value) to allow the specification of colours in a standardized format. As the colour intensity or colour hue can be proportional to the concentration of a chemical species, the quantification of this species can be performed from the correlation of colour coordinates [26]. The use of digital images has been widely reported for the quantification of several analyte types, for instance in food, pharmaceutical and biochemical [27].

Different capillary supports have been used for point-of-care devices that include the different analytical operations necessary to construct the analytical procedure for both the pretreatment and the detection of the sample. One of the analytical operations usually necessary in complex samples with low analyte concentrations is preconcentration in order to reach the concentration necessary for a reliable measurement of the analytical property. Different strategies have been devised to achieve preconcentration with paper or thread-based devices [28]. One such strategy is based on electrical interactions where the ion concentration polarization allows for the electrokinetic preconcentration of different molecules [29,30]. Another proposal is based on the use of isotachophoresis on nitrocellulose-based paper for preconcentration and the separation of lateral flow immunoassay (LFIA) tests [31]. A third strategy is based on the modification of the support with different chemical reagents. For instance, the modification of filter paper with zinc oxide nanorods was used to develop a paper-based ELISA device for myoglobin preconcentration [32]. The preconcentration using conventional reagents for metal ions combined by chemometric approaches makes it possible to identify 5 heavy metals [6,13]. Yet another system used for preconcentration combines the design of the paper device and a surface chemical gradient created by differential polyelectrolyte coating of the paper for preconcentration and identification [33].

This article describes a low-cost, simple and environmentally-friendly μTAD for the preconcentration and determination of trace amounts of Co(II) in tap water using immobilized PAR in a chitosan membrane.

2. Experimental

2.1. Reagents and materials

The solutions were prepared with reverse osmosis type quality water (Milli-RO 12 plus Milli-Q station (Millipore, Bedford, MA). All reagents were of analytical grade and were used as received without further purification. A cotton thread (12 calibre and 94 NTex) from Finca (Presencia Hilaturas S.A. Alzira, Valencia, Spain) measuring some 600 μm in diameter and containing 250 ± 10 fibres was obtained from a local store and used as the support for the fabrication of the μTAD. Passive pumps were fabricated with absorbent pads containing Flexicel® (P&G Spain, Madrid). A chitosan solution of 25 $mg{\cdot}mL^{-1}$ was prepared by dissolving 150 mg of high molecular weight chitosan in 6 mL of purified water containing 150 μL of glacial acetic acid for 30 min with the aid of a magnetic stirrer. The 4-(2-pyridylazo) resorcinol (PAR) solution $2.50{\cdot}10^{-3}$ $mol{\cdot}L^{-1}$ was prepared by dissolving 1.08 mg of the reagent in 2.0 mL of ethanol 99.9% (Panreac). Potassium dihydrogenphosphate anhydrous (Merck) and potassium monohydrogenphosphate anhydrous (Merck) were used to prepare the phosphate buffer solution (0.1 $mol{\cdot}L^{-1}$, pH 8.00). The solutions of Co (II) varying from 25 to 600 $\mu g{\cdot}L^{-1}$ were prepared by adding the appropriate volume of the stock solution of Co(II) 1000 $mg{\cdot}L^{-1}$ (Panreac) in volumetric flasks of 10 mL. For most of the studied interferents (Ni (II), Cd(II), Cr(III), Hg(II), Cu(II), Mn(II), Zn(II) and Pb (II)) the standard solutions (Panreac, 1000 $mg{\cdot}L^{-1}$) were employed. However, for Fe (II) and Fe(III), ammonium iron(II) sulfate hexahydrate (Merck) and iron(III) chloride anhydrous (Panreac) were used, respectively. Recovery studies were assessed by making spiked additions to a tap water sample collected from the water supply network of Granada (Spain). For comparison purposes an Agilent Technologies atomic absorption spectrometer, model 240 FS AA was employed.

2.2. Fabrication of the μTAD

The cotton thread was first cleaned by boiling in a solution of sodium carbonate 10 $g{\cdot}L^{-1}$ for 10 min. After that, the thread was washed with purified water until the washing water pH was neutral. Lastly, the thread was dried at room temperature and stored in a small, closed plastic bottle for further use.

The platform on which the thread is laid was designed using Illustrator software and engraved using a Rayjet Trotec Laser engraving printer (Trotec, Austria) using Rayjet Commander software. It consists of a piece of methacrylate, 0.4 cm high, 2.0 cm wide and 5.5 cm long, containing two types of well, one well for sampling and two for the passive pumping pad (Fig. 1). The sampling well is 0.5 cm diameter and 0.2 cm high with a round bottom. Before use, 10 μL of 0.1 $mol{\cdot}L^{-1}$ phosphate buffer (PB) pH 8.00 is placed in this well and allowed to dry. The pumping wells are 1.0 cm in diameter and 0.2 cm high with a flat bottom in which an absorbent pad (2 mm thick) cut into a 1 cm diameter circular shape with the laser printer is introduced.

Two pieces of scoured cotton thread (1.0 and 3.3 cm each) are located in the Y shape-path engraved in the methacrylate support. Lastly, 0.1 μL of $2.50{\cdot}10^{-3}$ $mol{\cdot}L^{-1}$ ethanolic solution of PAR is added to the cotton thread before the junction of the three arms of the Y, leaving it to dry for 5 min at room temperature. Then, 10 μL of 25 $mg{\cdot}mL^{-1}$ of aqueous chitosan solution is added, leaving it for 5 min at room temperature to complete the drying (Fig. 1).

2.3. Use and digitalization of the μTAD

To use the μTAD, 50 μL of sample or standard is added to the sampling well where the dried BP is reconstituted, adjusting the pH of the sample to 8. The sample wicks along the thread to the sensing area and 30 min later, the device is digitalized.

To acquire the μTAD's pictures, a Sony DSC-HX300 digital camera (Sony, Tokyo, Japan) was placed in a fixed position over the μTAD inside a cube light box illuminated by two LED bulbs (3000 K), producing a luminance at the stage of 165 lx and keeping the image-gathering conditions the same. The setting conditions used were: resolution of 3648 × 2736 pixels, aperture value f/3.5, exposure time 1/40 s, ISO-80, 2800 K white balance. The images were saved in jpg format (Joint Photographic Experts Group). The picture was analysed using the ImageJ (National Institutes Digital of Health) software,

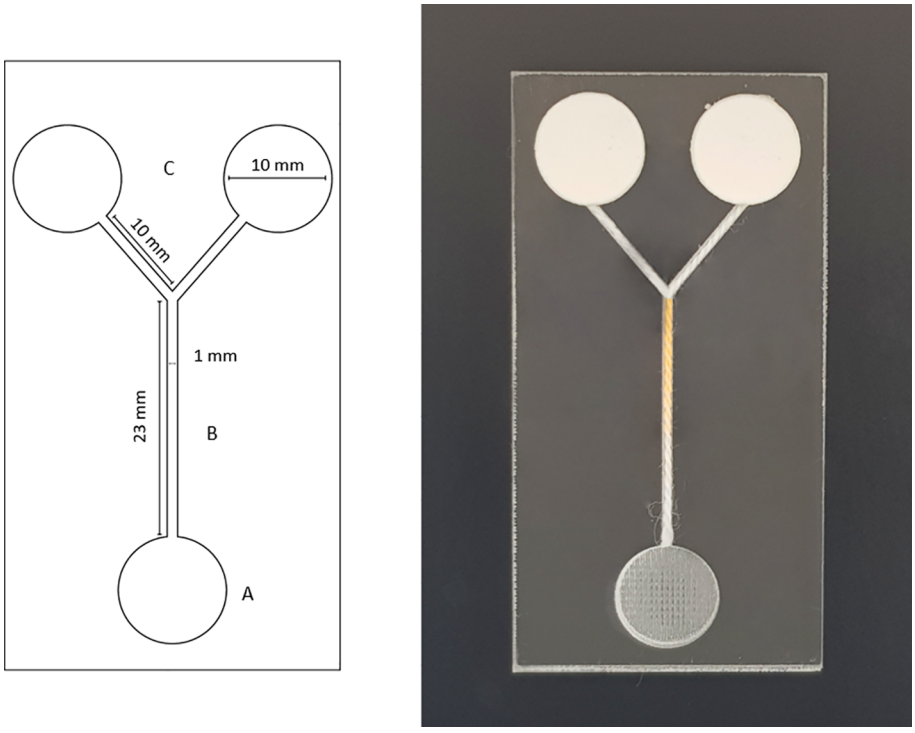

Fig. 1. Picture of the μTAD for Co(II): Left: μTAD design and dimensions composed by: A) sampling well; B) cotton thread and C) adsorbent pads; Right: Picture of μTAD ready to use.

marking the Region of Interest (ROI) (some 15,000 pixels) and analysing it in terms of colour coordinates, obtaining an average H parameter (HSV colour space) from the ROI pixels.

3. Results and discussion

In this work, we combine a chromogenic reagent for preconcentration and determination with a cotton thread modified with chitosan. Among *ortho*-hydroxy azo compounds, 4-(2-pyridylazo) resorcinol (PAR) stands out as a classic sensitive analytical reagent for metal ions, forming complexes with various ions from the d, p and f blocks of the periodic table that intensively change their spectral properties upon metal ion binding. Moreover, the solubility of PAR and its chelates in water has advantages over other widely used approaches such as 1-(2-pyridilazo)-2-naphtol (PAN).

The PAR molecule has three acid-base groups, the pyridyl group and two hydroxyl groups of resorcinol moieties. The most acidic group corresponds to the proton bound to the pyridinic nitrogen (pK_{a1} = 3.07 in water). *Ortho*-and *para*-hydroxyl present significant differences in acidity (pK_{a2} = 5.50; pK_{a3} = 12.04) due to the fact that the hydrogen bonding interaction of *ortho*-hydroxyl group with azo group reduces its acidity [34] (Fig. S1).

The reaction of PAR with Co(II) in aqueous solution requires a structural change, the breaking of the intramolecular hydrogen bond, the rotation of the resorcinol ring around the C-N bond by 180° and the deprotonation of *ortho*-hydroxyl group. After the initial formation of 1:1 and 1:2 (M:L) complexes, Co (II) quickly oxidizes to Co (III). The presence of the *para*-hydroxyl is due to the fact that, depending on the pH, the complex is positively charged at pH values of about 2 or less ($[Co(III)(HL)_2]^+$)($[Co(III)(HL)_2]^+$), negatively charged at pH of about 6 or higher ($[Co(III)L_2]^-$)and neutral in between ($[Co(III)L(HL)]^0$). This agrees with the average value for the two acidity constants of the complex, which is calculated to be 4.1 [35].

As material to prepare the μTAD, cotton thread was chosen due to its strong hydrophilicity, good absorbency and ability to move liquids by capillary action through the lumen of each fibre, the spaces between the fibres that constitute a yarn and the gaps between the yarns that constitute a thread. In preliminary tests, PAR was immobilized on the thread by sorption from an ethanolic solution, observing that when a solution of Co (II) in basic medium passes along the thread by capillary flow, the complex is not retained, but is carried by the flow. This fact is consistent with the anionic nature of the Co (III) complex in this medium.

To achieve immobilization and, thus, the preconcentration of the PAR-Co complex, chitosan, which is a biodegradable cationic aminopolysaccharide polymer derived from chitin by N-deacetylation, is selected to reduce leaching. The high percentage of reactive amino groups that it contains, allows it to convert it into a cationic polymer of hydrophilic character by protonation, due to the large number of hydroxyl groups present [36].

The μTAD designed for Co(II) determination is a single channel-type device made in thread with a sampling well at the beginning of the thread, preconcentration and a detection area containing the recognition chemistry and a double pumping area at the end (Fig. 1). The presence of chitosan where the retained PAR complex is found allows for the preconcentration of the cobalt complex, but with the disadvantage of considerably slowing down the flow. For this reason, two Y-shaped cotton threads were added, each ending in a pad of absorbent material to allow the sample to continuously pass through the recognition area and preconcentrate.

In this μTAD, the analytical parameter comes from the reagent colour change, PAR, from yellow (H = 0.133) to red–purple of the Co (III) complex (H = 0.071), obtained from a photograph of the device. The extension of the colour change from yellow to red–purple, measured by the colour coordinate H, from the HSV colour space, is related to the analyte concentration [26].

3.1. Reaction parameters

Different variables were studied and optimized to adjust the PAR reaction to the μTAD format. For the recognition and transduction reaction, the on-thread PAR immobilization, the amount of PAR and the

pH adjustment were all optimized. For the preconcentration process, the amount of chitosan, equilibration time and volume of sample were studied.

First, the appropriate size of the recognition zone, where PAR was immobilized by adsorption, was studied to define the ROI and make it possible to obtain a reproducible analytical parameter. It was found that depositing 0.1 μL of $5{\cdot}10^{-3}$ mol·L^{-1} ethanolic solution of PAR on cotton thread is enough to prepare a zone of 0.8 ± 0.1 cm long for cobalt preconcentration without excessively increasing the time necessary for the sample to pass through and producing an ROI of about 15,000 pixels.

As indicated above, the cobalt complex is not well retained on the thread due to its anionic nature, but is partially dragged through the thread. The addition of chitosan over the PAR in the recognition zone makes it possible to retain the cobalt complex, thus improving the homogeneity of the ROI [37]. Chitosan was selected because it is well retained on cloth [38], thread [36] and also on paper [39].

We use a 25 mg·mL^{-1} chitosan solution, because it is the most concentrated solution that can be reproducibly prepared, in order to use the smallest possible volume of chitosan solution that covers the transduction zone and does not spread along the thread. Volumes of 5, 10 and 15 μL of 25 mg·mL^{-1} chitosan solution were studied. A volume of 10 μL volume was chosen for subsequent studies, since 5 μL is not sufficient to cover the recognition zone, reducing the homogeneity of the ROI, and 15 μL affects the wicking properties of the thread, increasing the analysis time and reducing the precision of results. The use of 10 μL of chitosan solution is sufficient to form a membrane (see Fig. S2) to cover all the PAR area and improves the retention of the anionic complex by cationic polymer, increasing the homogeneity of the ROI and thus improving the reproducibility (from 8.3% CV without chitosan to 2.5% with it, n = 3).

The influence of PAR concentration was studied by adding 0.1 μL PAR solution from $1.0{\cdot}10^{-3}$ to $7.5{\cdot}10^{-3}$ mol·L^{-1} and calculating the H value after reaction with 200 μg·L^{-1} Co(II) (Fig. S3). We observed that ΔH (H_{PAR}-$H_{PAR\text{-}Co}$) increases up to $2.5{\cdot}10^{-3}$ mol·L^{-1} remaining constant after this point, and selected this concentration as optimal.

It is well known that the equilibrium between Co(II) and the PAR is affected by pH, with 9 being the optimum in the solution [40]. The effect of pH on the analytical signal was studied between 6.0 and 10.0 (n = 3) (Fig. 2), observing that at high pH the formation of the PAR complex is facilitated due to the deprotonation of the reagent, with the optimum pH being 8.0.

In order to achieve the preconcentration of Co(II), the volume of the analyte solution must pass through the area where the PAR is located. The presence of chitosan in that area causes the assay to slow down. To reduce the analysis time, two almost 0.16 cm^3 passive pumps manufactured out of superadsorbent material are used to move the solution. They are connected by two pieces of thread on both sides of the reaction zone. Volumes of 200 μg·L^{-1} Co (II) solution in the range of 10 to 100 μL were studied, monitoring the evolution of H values up to 40 min. As Fig. 3 shows, the H signal increases with the sample volume up to 50 μL, because at higher volumes, the reproducibility of the preconcentration process decreases. The reaction time needed for equilibration was studied using 50 μL of the sample and different Co(II) concentrations (n = 3), with the result that 30 min are needed to obtain stable signals (Fig. S4). Therefore, 30 min was selected.

3.2. Analytical parameters and enhancement factor

Once the μTAD was optimized, it was characterized by its analytical parameters. The μTAD was calibrated using ten different cobalt standard solutions from 25 to 600 μg·L^{-1} (n = 5). The relationship between the H parameter and cobalt concentration (μg·L^{-1}) is linear (Fig. 4), obtaining the equation: $H = -1.26{\cdot}10^{-4}\cdot [Co(II)] + 0.134$, with a R^2 of 0.977 and a standard deviation of 0.001 and $7{\cdot}10^{-6}$ for the intercept and slope, respectively.

The μTAD procedure is characterized by a limit of detection (LOD) of 6.5 μg·L^{-1}, a limit of quantification (LOQ) of 21.5 μg·L^{-1} and a range between 21.5 and 600 μg·L^{-1} (0.37–10.18 μM). The precision was studied at two levels (50 and 300 μg·L^{-1}), obtaining relative standard deviations around 4% for both concentrations (n = 10).

When a preconcentration step is included in an analytical procedure method, the enhancement factor is calculated to quantify its performance. This factor is defined as the ratio of the slopes of the calibration function including the preconcentration step and the slope when there is no preconcentration step [41]. The slopes used for the calculation were the slope from the calibration function of the developed μTAD when preconcentration is carried out, and the slope of the calibration of the μTAD when there is no preconcentration process.

To obtain the slope without preconcentration, the μTAD had no chitosan to retain the PAR-Co complex, and no adsorbent pads to move a high volume of the sample. The volume used was 3 μL, the higher volume that does not drag the PAR or PAR-Co complex through the thread, thus obtaining reproducible results. In this case the enhancement factor obtained was 11.

The selectivity due to the presence of other metal ions in the sample,

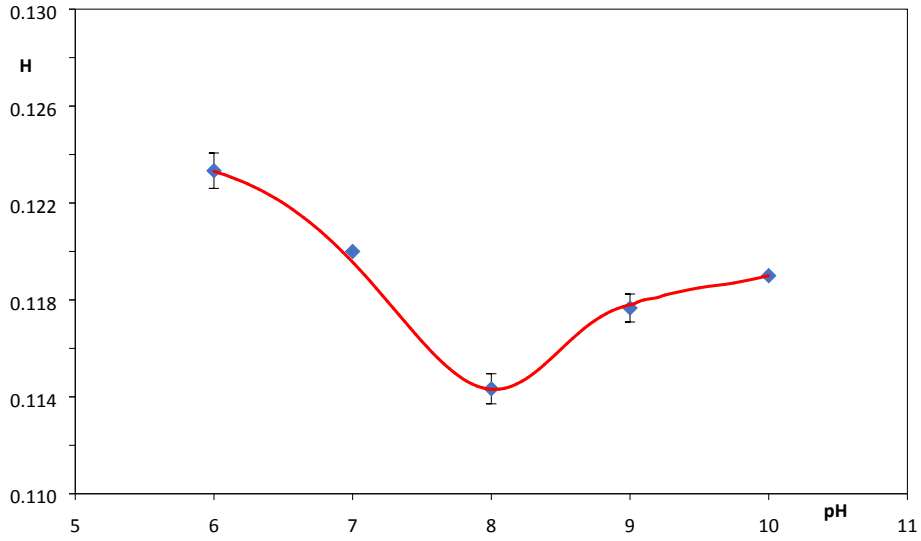

Fig. 2. Hue (H) coordinate evolution of the μTAD with pH.

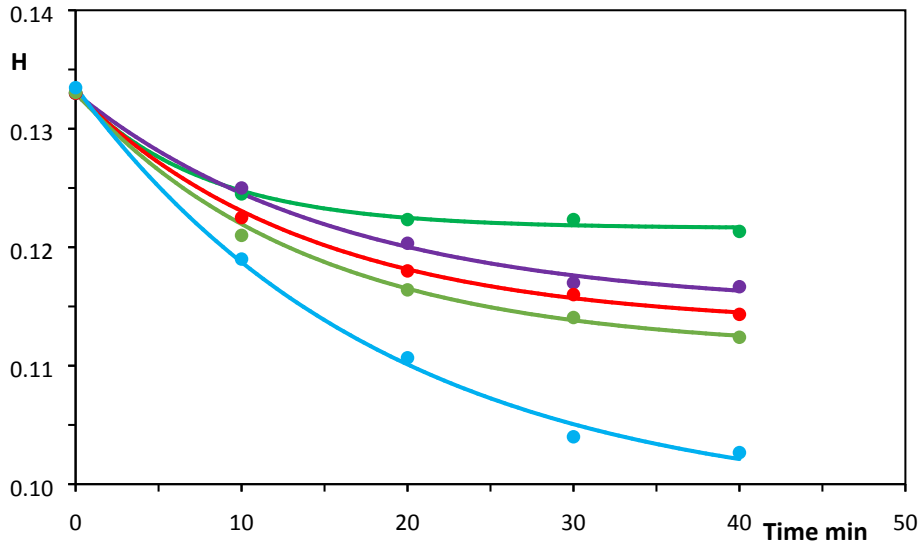

Fig. 3. Influence of volume of Co(II) standard solution (200 μg·L^{-1}) on equilibration. Volumes tested: 10 (green), 15 (purple), 25 (red), 35 (orange) and 50 μL (blue) (n = 3).

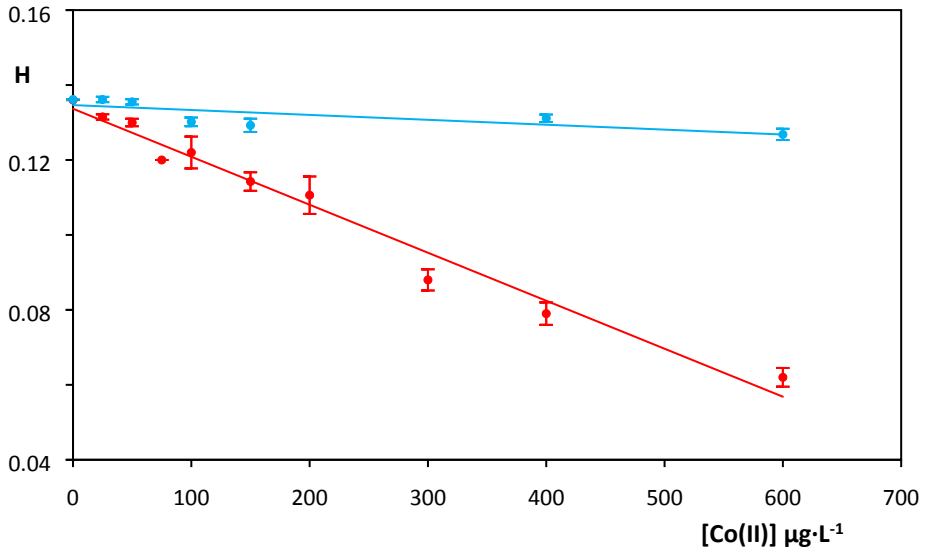

Fig. 4. Calibration function of μTAD with preconcentration (red dots) and without preconcentration (blue dots) (n = 5).

such as Ni(II), Cd(II), Cr(III), Hg(II), Cu(II), Mn(II), Zn(II), Pb (II), Fe(II) and Fe(III), was studied. For this purpose, mixtures containing Co(II) (200 μg·L^{-1}) and each interferent (200 μg·L^{-1}) were tested, obtaining the results in Fig. 5. The signal variation due to the presence of the metals is less than 5%. Only in the case of Fe(III) was it higher (8%), but with the inclusion of 0.5 μL of 0.1 M sodium fluoride in the detection zone, the interference is reduced (1.8%) due to the masking of the Fe (III). This is probably because Fe(III) forms a more stable complex with fluoride than with PAR.

The selectivity found for Co (II) is attributed to several factors. On the one hand, because Co (II) rapidly originates a 2:1 stoichiometry complex that is oxidized by atmospheric oxygen to Co (III), resulting in a complex with a negative charge at the working pH [42]. This complex is retained by chitosan immobilized on the cotton thread, which acts as a cationic polymer. The neutral divalent metal complexes will be dragged by the flow imposed by the passive capillary pump included in the device. This, in turn, justifies the Fe (III) interference for the same reason, interference that can be reduced by masking Fe (III) with fluoride. On the other hand, the small interference of Cr (III) is due to the inertia of its aquocomplex, which translates into a low reaction rate [43,44], being consequently dragged by the sample flow. Finally, it must be considered that the amount of PAR immobilized in the thread is small, which makes it difficult to retain complexes with less stability.

3.3. Application of μTAD in tap water samples

In order to test the capabilities of the proposed device, spiked samples (50, 100, 150, 200, 250 and 300 μg·L^{-1} Co(II)) of tap water samples obtained from the water supply network of Granada (Spain) were analysed and results compared to the obtained a reference method, atomic absorption spectroscopy. Table S1 shows the errors in the determination, never higher that 5.7%. These results suggest that the proposed colorimetric μPAD can be used for the determination of cobalt in real samples with low error compared to the reference method and reasonable precision.

4. Conclusion

The proposed one-step assay presents an interesting alternative to the usual methods for the determination of elements at low

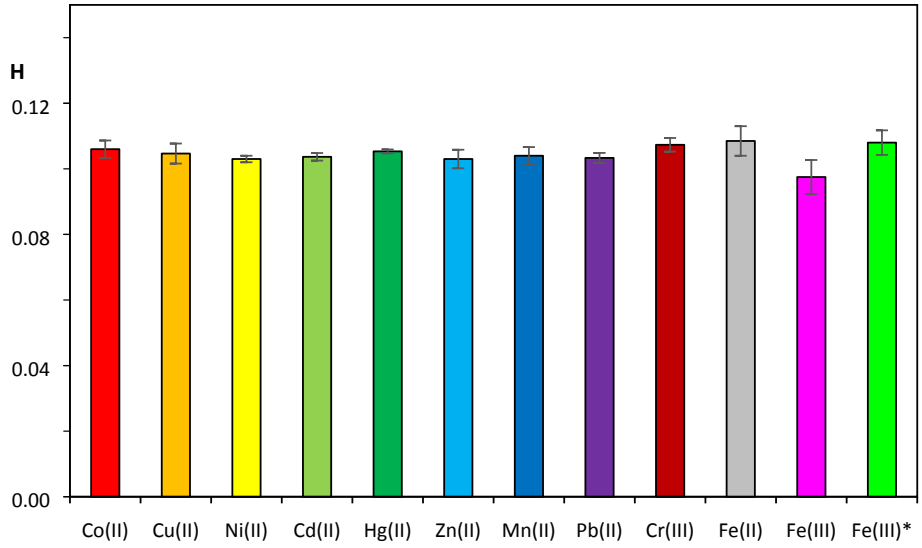

Fig. 5. Selectivity of μTAD for Co(II) (200 $\mu g \cdot L^{-1}$) for different metal ions in 1:1 M ratio. In the case of Fe(III)* 0.5 μL of 0.1 M sodium fluoride was included in the detection zone (n = 3).

concentrations. It is an efficient method that maintains the simplicity and low cost of methods that involve digital image analysis, but extends its possibilities of application with increasing sensitivity through the use of chitosan to immobilize the chromogenic reagent. The association between cotton thread, the cationic hydrophilic polymer chitosan, a superadsorbent polymer and the chromogenic azo dye PAR provided a significant increase in the sensitivity for the determination of Co(II) in water. The μTAD is able to preconcentrate (enhancement factor of 11) and determine Co(II) (LOD of 6.5 $\mu g \cdot L^{-1}$; 110 nM) in tap water with moderate error (no higher than 5.7%) and precision (some 4% at the tested concentrations). In comparison to methods described in the literature that use microdevices, it offers a higher versatility, simplicity of operation and sensitivity to quantify low levels of Co(II) (Table S2). Additionally, the proposed method is environmentally-friendly generating low waste, with low toxicity reagents and a very low cost, less than €0.01 per device. Furthermore, the developed method offers an innovative alternative for the determination of Co(II), and it can be performed using a conventional digital camera.

CRediT authorship contribution statement

Willian Toito Suarez: Formal analysis, Conceptualization, Methodology, Writing - original draft, Funding acquisition, Investigation, Visualization, Supervision. **Mathews O.K. Franco:** Formal analysis, Visualization, Writing - original draft. **Luis Fermín Capitán-Vallvey:** Conceptualization, Methodology, Writing - original draft, Funding acquisition, Resources, Project administration. **Miguel M. Erenas:** Formal analysis, Conceptualization, Methodology, Writing - original draft, Investigation, Visualization, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Compliance with ethical standards

The authors declare that they have no competing interests.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2020.105137.

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