



# Bromine speciation by a paper-based sensor integrated with a citric acid/cysteamine fluorescent probe and smartphone detection

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## ABSTRACT

The present work reports on a sensitive and affordable non-instrumental method for the determination of bromine species in environmental waters by combination of paper-based headspace sampling and smartphone-based fluorescence detection. The proposed approach takes advantage of the luminescence quenching of a probe (5-oxo-3,5-dihydro-2 H-thiazolo[3,2-a]pyridine-7-carboxylic acid, TPCA) derived from natural compounds, namely, citric acid and cysteamine, when exposed to molecular bromine. The decreased luminescence intensity of the probe was attributed to the formation of a dibrominated derivative of TPCA at the detection area of a paper-based analytical device (PAD). Remarkably, PADs modified with the luminescent probe showed excellent stability. Under optimal conditions, the proposed approach showed limits of detection of  $5.4 \mu\text{g L}^{-1}$  and  $0.9 \mu\text{g L}^{-1}$  for  $\text{Br}^-$  and  $\text{BrO}_3^-$ , respectively, with a repeatability lower than 10% for both bromine species. The non-instrumental method was validated against two certified reference materials, namely BCR-611 and BCR-612 (low and high level  $\text{Br}^-$  in groundwater), and successfully applied to the analysis of environmental water samples with recoveries in the range 93–106%.

## 1. Introduction

Bromine speciation analysis in environmental samples is receiving increasing attention in recent years [1].  $\text{Br}^-$  concentrations ranging from  $65 \text{ mg L}^{-1}$  to  $80 \text{ mg L}^{-1}$  have been reported in sea water, whereas concentrations of this anion mostly range from trace amounts to  $0.5 \text{ mg L}^{-1}$  in fresh water [2]. Even though  $\text{Br}^-$  shows very low toxicity, several studies have confirmed its major role in the unintended formation of a series of highly toxic brominated disinfection by-products (DBPs) when water samples are subjected to different oxidation processes [3–6]. Thus,  $\text{Br}^-$  monitoring can be particularly important to prevent or minimize the formation of hazardous DBPs.  $\text{BrO}_3^-$  is a potential human carcinogen [7] that is not commonly monitored in waters, yet it can be formed as a by-product of water disinfection at levels as high as ca.  $300 \mu\text{g L}^{-1}$  [2]. Together with other DBPs such as chlorite, haloacetic acids and trihalomethanes,  $\text{BrO}_3^-$  concentrations in drinking water are regulated by the USEPA, with a maximum contaminant level of  $10 \mu\text{g L}^{-1}$  [8]. The development of sensitive analytical strategies to cope with such stringent regulations is thus an imperative priority. A number of analytical methods have been reported in the literature for bromine speciation in environmental waters, including ion chromatography and

high performance liquid chromatography combined with inductively coupled plasma mass spectrometry [9], gas chromatography-mass spectrometry [10,11], dielectric barrier discharge-optical emission spectrometry [12] and flow injection with long path length spectrophotometry [13]. These methods are robust and their low limits of detection allow the compliance with the established regulations. However, they commonly involve the use of sophisticated and expensive equipment. The development of low-cost, sensitive and straightforward strategies for bromine speciation is particularly desirable. In this sense, paper-based analytical devices (PADs) are promising alternatives for environmental analysis. Their inexpensiveness, facile fabrication and convenient combination with a variety of information technology and communications equipment make them extremely valuable for sensing purposes [14–19]. In spite of the undeniable advances achieved in the field, the number of contributions devoted to the determination of inorganic species is still limited, and commonly lack enough sensitivity and selectivity [20,21]. In this sense, the implementation of modified PADs in headspace microextraction approaches has enabled the enrichment and optical detection of some inorganic species by *in situ* volatile generation [22–28]. Colorimetric sensing is, by far, the most common strategy with PADs, whereas fluorimetric sensing is less

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exploited in spite of its remarkable sensitivity and selectivity. In this sense, it is worth mentioning that the fluorimetric detection of bromine species has barely been explored, involving luminescent molecular probes (e.g., fluorescein and carbostyryl-124) [29–31] and carbon nanodots [32]. Particularly, there is a growing interest in the implementation of both natively emissive natural products and luminescent probes derived from natural compounds, such as carbon nanodots, in a broad variety of applications [33–36]. Recently, it has been revealed that the high luminescence of citric acid-derived carbon nanodots can be attributed to organic fluorophores formed by reaction between citric acid and certain natural amines and amino acids [37–43]. Thus, the synthesis of a particularly attractive fluorophore derived from citric acid and cysteamine, namely 5-oxo-3,5-dihydro-2 H-thiazolo[3,2-*a*]pyridine-7-carboxylic acid (TPCA), by both one-pot reaction [41,44,45] and hydrothermal synthesis [43], has been reported in the literature. In general terms, citric-acid derived luminescent materials display excellent optical properties and their incipient implementation in PADs [25, 45,46] seems to indicate that could open up new prospects for sensing purposes.

The present work reports, for the first time, on the suitability of TPCA for Br<sub>2</sub> sensing purposes. Based on this finding, a smartphone-based fluorimetric sensing approach was devised for non-instrumental bromine speciation analysis on the basis of the luminescence quenching that occurs when PADs modified with the luminescent probe were exposed to the volatile. The reported sensing strategy enabled the sensitive and selective determination of bromine species, namely Br<sup>-</sup> and BrO<sub>3</sub><sup>-</sup>, in environmental samples at concentration levels below the guideline values set by the World Health Organization. As far as we are aware, this is the first contribution reporting on the applicability of citric acid derived fluorophores for speciation studies.

## 2. Experimental

### 2.1. Reagents

All reagents were of analytical reagent grade. High-purity deionized water was obtained from a Millipore Sigma Simplicity ultrapure water system (Millipore Iberian S.A., Madrid, Spain). Citric acid monohydrate and cysteamine hydrochloride (Sigma-Aldrich, St. Louis, MO, USA) were used for preparing the fluorophore. Stock standard solutions of Br<sup>-</sup> (4000 mg L<sup>-1</sup>) and BrO<sub>3</sub><sup>-</sup> (1000 mg L<sup>-1</sup>) were prepared from potassium bromide (Merck, Darmstadt, Germany) and potassium bromate (Panreac, Barcelona, Spain), respectively. Working standards were daily prepared by suitable dilution of stock solutions with ultrapure water. The following reagents were also used: sodium nitrite and sodium sulfide from Panreac (Barcelona, Spain), sodium sulfate, potassium iodide, potassium iodate, iron(III) nitrate nonahydrate, copper and zinc from Merck (Darmstadt, Germany), potassium chloride, sodium chloride, potassium nitrate, sodium hypochlorite and sulfuric acid from Prolabo (Paris, France), sodium phosphate from Sigma-Aldrich (St. Louis, MO, USA), sodium hydrocarbonate from Carlo Erba (Milan, Italy), and humic acid from Fluka Chemie (Buchs, Switzerland).

### 2.2. Apparatus and materials

The chemical structure of TPCA before and after exposure to vapor bromine was characterized by <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) and high-resolution mass spectroscopy (HR-MS). A Bruker Avance DPX400 spectrometer (Bruker, Billerica, Massachusetts, USA) was employed to acquire <sup>1</sup>H and <sup>13</sup>C NMR spectra using DMSO-d<sub>6</sub> as solvent. HR-MS was conducted using a microTOF (focus) mass spectrometer (Bruker Daltonics, Bremen, Germany) with electrospray ionization (ESI). A Cryodos-50 freeze dryer (Telstar, Terrasa, Spain) was used before the characterization of TPCA. A Horiba Fluoromax-4 spectrofluorometer (Horiba Scientific, Edison NJ, Tokyo, Japan) was used to record fluorescence spectra of TPCA.

Whatman No. 1 filter paper from Whatman (Maidstone, Kent, UK) and a Lumocolor permanent pen 318-9 fine 0.6 mm (Staedtler, Nuremberg, Germany) were used for the preparation of PADs. Alternatively, a Xerox ColorQube 8580 printer (Rochester, New York, USA) and a Phoenix instrument RSM-02HP+ magnetic stirring hot plate (Garbsen, Germany) were used for defining hydrophobic barriers on Whatman No. 1 filter paper by wax printing technology [47]. A Huawei P8 Lite 2017 smartphone (Huawei, Shenzhen, China) and a C-10 Chromato-Vue mini UV viewing cabinet (265 × 235 × 225 mm) (Analytik Jena, Jena, Germany) equipped with an UVP handheld UV lamp (198 × 71 × 53 mm, 4 watt lamp, 254/365 nm) (The Science Company, Lakewood, CO, USA) were used for smartphone-based fluorescence detection.

### 2.3. Data processing

The free image processing program ImageJ was used for non-instrumental data acquisition [48]. Alternatively, the App RGB Color Detector (The Programmer, Google Play Store) was used with this aim with the smartphone camera. These tools were used to measure the mean color intensity of the detection area of PADs in the corresponding RGB channel. The statistical package Statgraphics Centurion XVI.I (StatPoint Technologies, Warrenton, VA, USA) was employed for optimization of experimental conditions.

### 2.4. Synthesis of TPCA

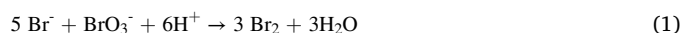
TPCA was obtained *via* solvent-free one pot reaction following a previously reported procedure [41] using cysteamine hydrochloride instead of cysteamine, as reported in an alternative hydrothermal method [43]. In brief, 2.1 g of citric acid and 1.13 g of cysteamine hydrochloride were placed in a round bottom flask and heated at 150 °C for 2 h. The resulting product was filtered and purified by recrystallization with ultrapure water. After that, the solution was stored in amber vials at 4 °C prior to use.

### 2.5. Preparation of PADs

Square shaped hydrophobic barriers with a side length of 6 mm were defined in Whatman No. 1 filter papers either by wax printing or manually by means of a permanent marker, following fabrication processes reported in the literature [22,47,49]. Subsequently, modified cellulose substrates were cut into 20 mm-diameter circular pieces containing a single hydrophilic detection area delimited by hydrophobic barriers. Then, 4.0 μL of a TPCA solution (diluted 10-fold and adjusted to pH 6.0) was deposited on the detection area of each PAD. The as-prepared PADs were dried in air protected from the light and stored in the desiccator prior to use.

### 2.6. Experimental procedure for bromine sensing

10 mL of blank, standard or sample solutions containing 1.5 M H<sub>2</sub>SO<sub>4</sub> were placed into 40 mL amber vials containing PTFE-coated stir bars (15 × 6 mm) and sealed with screw caps with septa. PADs prepared as described in Section 2.5 were then placed over the septa and exposed to the headspace. After closing the vials, 1 mL of 10 mM KBrO<sub>3</sub> (for Br<sup>-</sup> determination) or 1 mL of 10 mM KBr (for BrO<sub>3</sub><sup>-</sup> determination) was injected for *in situ* bromine generation in accordance with the reaction:



TPCA-containing PADs were exposed to the headspace above the aqueous solutions stirred at 1500 rpm for 30 min. Once the extraction process was accomplished, PADs were placed in a dark viewing cabinet and exposed to UV light (365 nm) to digitize the detection areas of PADs by a smartphone camera. Digital images were opened in ImageJ, inverted, and the mean color intensity of the selected detection areas

acquired using the B channel.

### 3. Results and discussion

#### 3.1. Evaluation of experimental parameters

In preliminary experiments, TPCA-containing cellulose substrates were exposed to a variety of volatiles and the obtained results revealed that the luminescent probe showed promising prospects for vapor bromine sensing. Unlike what was observed in the presence of volatiles derived from other anions, namely, chloride, iodide, nitrite, sulfite and sulfide, a significant quenching of the fluorescence of TPCA occurred in the presence of vapor bromine (Fig. S1). Accordingly, a method for bromine speciation analysis involving *in situ* bromine generation, mass transfer of the volatile and its trapping/reaction by TPCA-modified PADs with subsequent smartphone-based fluorescence detection was devised. Bearing in mind that  $\text{Br}_2$  is the common volatile for determination of both  $\text{Br}^-$  and  $\text{BrO}_3^-$  (1), and for the sake of avoiding redundancy, an experimental design was firstly used for  $\text{Br}^-$  determination, and optimal conditions were subsequently employed for  $\text{BrO}_3^-$  determination with the exception that an excess of  $\text{Br}^-$  was required (as reducing agent) for  $\text{Br}_2$  generation. Experimental parameters, including variables that show an effect on the vapor generation, mass transfer and digitization process, were evaluated and the obtained results are shown in this section.

##### 3.1.1. Assessment of digitization conditions

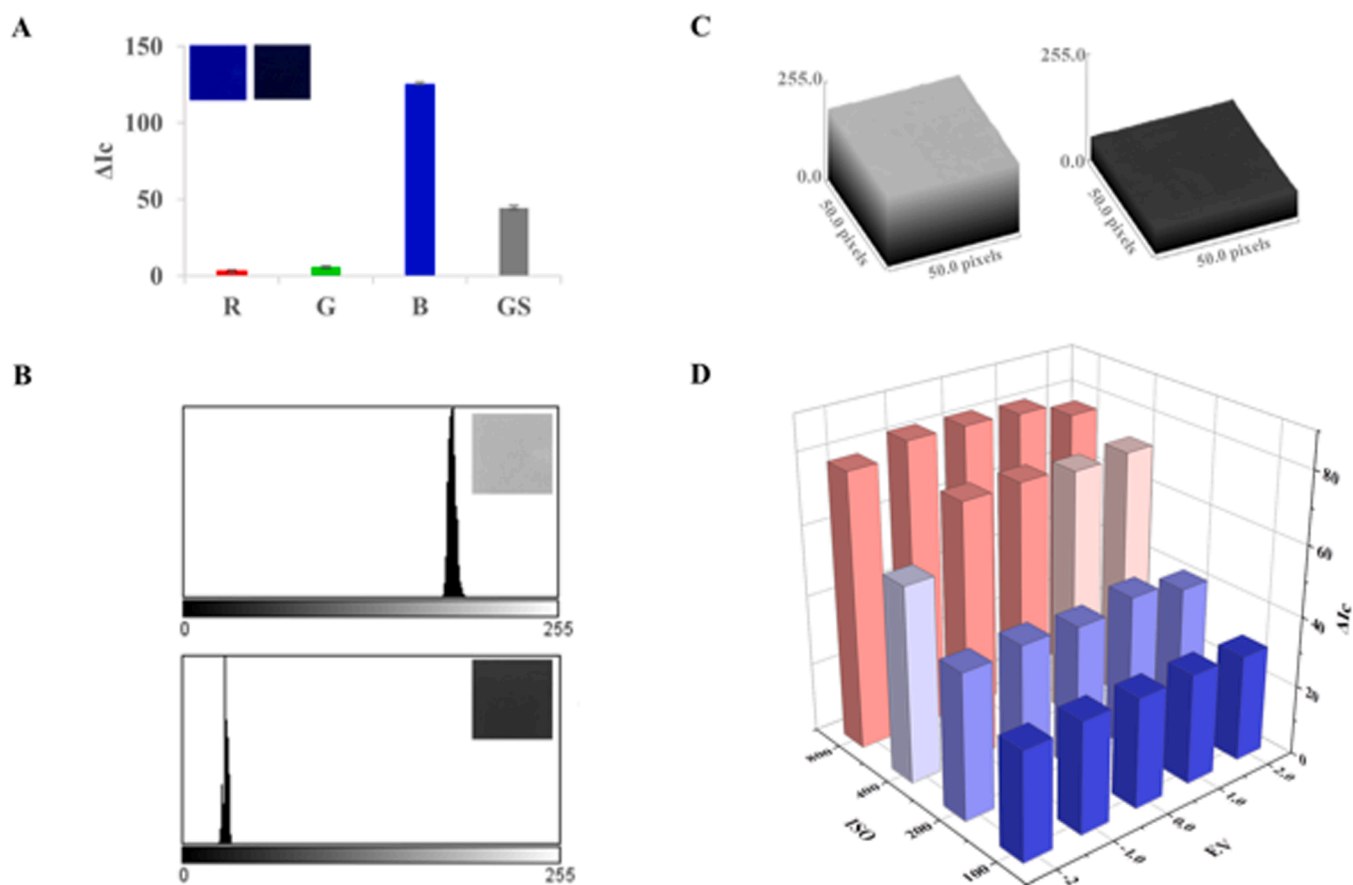
Several digitization-related variables can show a paramount effect over the analytical response, and therefore, they need to be carefully evaluated for non-instrumental bromine sensing. TPCA-modified PADs

(exposed to UV light at 365 nm) were digitized before and after exposure to vapor bromine, and the analytical signals in RGB and grayscale modes were acquired. As shown in Fig. 1A, the B channel led to the highest response, so it was selected for subsequent studies. The change in color intensity is noticeable in Fig. 1B, which shows the color intensity histograms corresponding to TPCA-containing PADs before and after their exposure to bromine. It can be noted that the color intensity is homogeneously distributed in the detection area, as shown in the surface plots depicted in Fig. 1C. The effect of digitization parameters, namely, sensitivity of camera's sensor (ISO) and exposure value (EV) were then assessed. ISO is referred to the sensitivity of the sensor to capture light, whereas EV relates exposure time and camera lens aperture. As can be observed in Fig. 1D, the analytical response (mean color intensity difference in the blue channel,  $\Delta Ic$ ) significantly increased with increasing ISO, whereas the effect of EV on the analytical response was found to be far less pronounced. Thus, digitization of PADs was carried out by setting the ISO and EV at 800 and +0.0, respectively, for optimal performance. The effect of the distance between the UV lamp and the PAD over the analytical response was also studied, but no significant differences were observed in the evaluated range (9.5–21.5 cm).

In addition, the effect of the dimensions of the PAD detection area and the concentration of TPCA on the analytical response was evaluated, and the obtained results are shown in Fig. S2. It can be deduced from the figure that the highest response ( $\Delta Ic$ ) was achieved when PAD detection areas in the range 6–8 mm and a TPCA concentration of 4.56  $\mu\text{M}$  (*i.e.* 10-fold dilution of the obtained fluorophore), respectively, were used.

##### 3.1.2. Screening of experimental parameters: PB design

A Plackett-Burman (PB) design was used to screening the main parameters involved in this study. Eight experimental parameters, namely,



**Fig. 1.** Effect of the color mode detection (RGB and grayscale, GS) on the analytical signal (A). Histograms of color intensity in the blue channel before and after exposure to vapor bromine (B) and the corresponding surface plots (C). Effect of EV and ISO on the analytical response (D).

drying time, extraction time, stirring rate, sodium sulfate concentration,  $\text{KBrO}_3$  concentration, sulfuric acid concentration, sample temperature and pH of the TPCA solution, were evaluated (Table S1). Additionally, three dummy variables were considered to estimate the experimental error [50]. According to the Pareto chart shown in Fig. 2, sulfuric acid concentration, sodium sulfate concentration and extraction time were statistically significant variables with a 95% confidence interval. Sodium sulfate caused a significant negative interferent effect over the analytical signal that could be ascribed to the high concentration levels typically used to improve mass transfer of volatiles by salting out effect, as reported in the literature [51]. Therefore, the addition of sodium sulfate to the sample was not considered. As was expected, sulfuric acid concentration caused a significant positive effect on the analytical signal, this acid playing a major role in the efficient *in situ* generation of vapor bromine. The remaining experimental variables were found to be non-statistically significant with a 95% confidence interval, as shown in Fig. 2. The pH of the TPCA solution showed a non-significant positive effect that could be ascribed to the different luminescent properties of TPCA at pH values above or below its  $\text{pK}_a$  value. In fact, the excitation maximum of TPCA at pH 6 (*i.e.*, the anionic form of TPCA) match well with the excitation wavelength used (365 nm), unlike TPCA at  $\text{pH} < \text{pK}_a$ , which suffers a blue-shift of the excitation maximum [25]. In addition, the effect of  $\text{KBrO}_3$  concentration, used as weak oxidizing agent for  $\text{Br}_2$  generation, was found to be positive even though non-significant for a confidence level of 95%. The three remaining variables, namely drying time, temperature and stirring rate, showed minimal effects. Based on the above, sulfuric acid concentration and extraction time were selected for the optimization of the method, whereas the rest of experimental conditions were selected at the most convenient levels, *i.e.*,  $\text{KBrO}_3$  concentration, 10 mM; sodium sulfate concentration, 0% (m/v); temperature, 23 °C (room temperature); drying time, 10 min; pH, 6.0; and stirring rate, 1500 rpm.

### 3.1.3. Optimization of experimental parameters: CCD design

A central composite design (CCD) comprising 16 experimental runs (Table S2) was applied to optimize the above-mentioned significant experimental parameters and to evaluate the main effect, the interaction between variables and the quadratic effect. As can be inferred from the Pareto chart (Fig. 3A), the evaluated experimental parameters, *i.e.*, extraction time and sulfuric acid concentration, showed positive significant effects with a confidence interval of 95%, whereas the quadratic effects and the interaction effect between the two variables were found to be negative and statistically significant. Fig. 3B shows the surface response as a function of sulfuric acid concentration and extraction time. An increase of both parameters caused an enhancement in the analytical response due to the efficient bromine generation and mass transfer process, respectively. Finally, an extraction time of 30 min and a sulfuric acid concentration of 1.5 M were selected as a compromise between sensitivity, sample throughput and consumption of reagents.

### 3.2. Characterization of TPCA in the absence and presence of bromine

To get into a feasible sensing reaction between TPCA and bromine, the luminescent probe was characterized by fluorescence spectroscopy,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and HR-MS before and after exposure to bromine (Figs. S3–S6). Fig. S3 shows the fluorescence emission spectra of TPCA in the absence and presence of the volatile. TPCA exhibited excellent fluorescence emission at 424 nm, being significantly quenched when exposed to the halogen. The HR-MS of TPCA (Fig. S4A) showed a molecular ion peak at  $m/z$  198 ( $[\text{M} + \text{H}]^+$ ), which is consistent with the literature data [44], whereas the molecular ion peak at  $m/z$  356 ( $[\text{M} + \text{H}]^+$ ) obtained after exposing TPCA to vapor bromine confirmed the presence of two bromine atoms in the molecule (Fig. S4B). The chemical structure of TPCA was also confirmed by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR (Figs. S5 and S6, respectively). The  $^1\text{H}$  NMR spectra of TPCA exposed to the halogen (Fig. S5) is attributed to the substitution of H atoms (CH, pyridine) at  $\delta$  6.52 and 6.56 by Br atoms. The  $^{13}\text{C}$  NMR spectra also confirmed this substitution, thus modifying the chemical shift of carbon atoms close to those positions (Fig. S6). According to the above, an electrophilic aromatic substitution presumably occurs at the pyridine ring [52], as depicted in Fig. 4.

### 3.3. Storage stability of TPCA-modified PADs

The applicability of TPCA-modified PADs depends to a large extent on the stability of the luminescent probe in the cellulose substrate PADs. Thus, the effect of storage time on the analytical response of TPCA-containing PADs was evaluated before and after their exposure to bromine. The stability of TPCA-modified PADs stored (protected from light) under four different conditions (room temperature (protected (desiccator) and unprotected from humidity); 4 °C (refrigerator) and –20 °C (freezer)) was assessed for 30 days. The mean color intensity ( $I_c$ ) of the detection area of TPCA-containing PADs was not significantly affected in the evaluated period when stored under the evaluated conditions (Fig. 5A). After storing for a month, analytical signals were found to be in the range of 95–102% as compared to freshly prepared PADs, regardless the storage conditions.

In addition, the analytical response ( $\Delta I_c$ ) was not significantly affected when PADs were used for bromine sensing after being stored for 30 days under four different conditions (Fig. 5B). Furthermore, the product formed at the detection area of the PAD upon exposure to bromine was found to be highly stable. In fact, the analytical response of PADs stored after exposure to vapor bromine was not significantly affected after 30 days of storage (Fig. 5C).

The remarkable stability of PADs (before and after exposure to vapor bromine) offers several practical advantages, including the potential for upscale production of PADs as well as the possibility to separately perform on-site microextraction experiments and subsequent non-instrumental analyses with no significant decline in the analytical response.

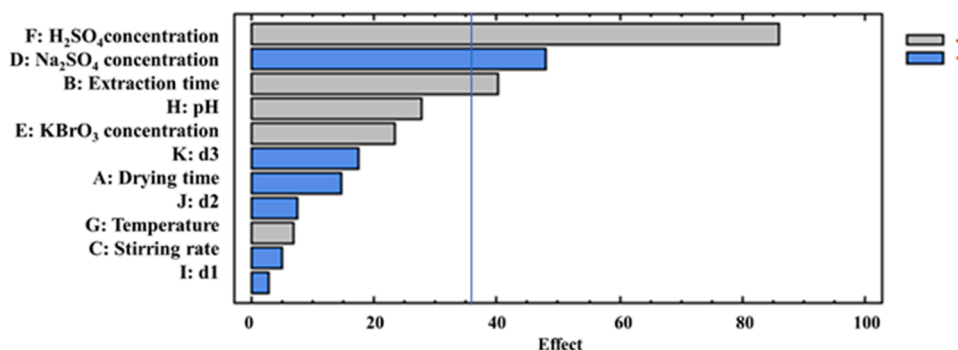


Fig. 2. Pareto chart of the main effects obtained from the PB design.

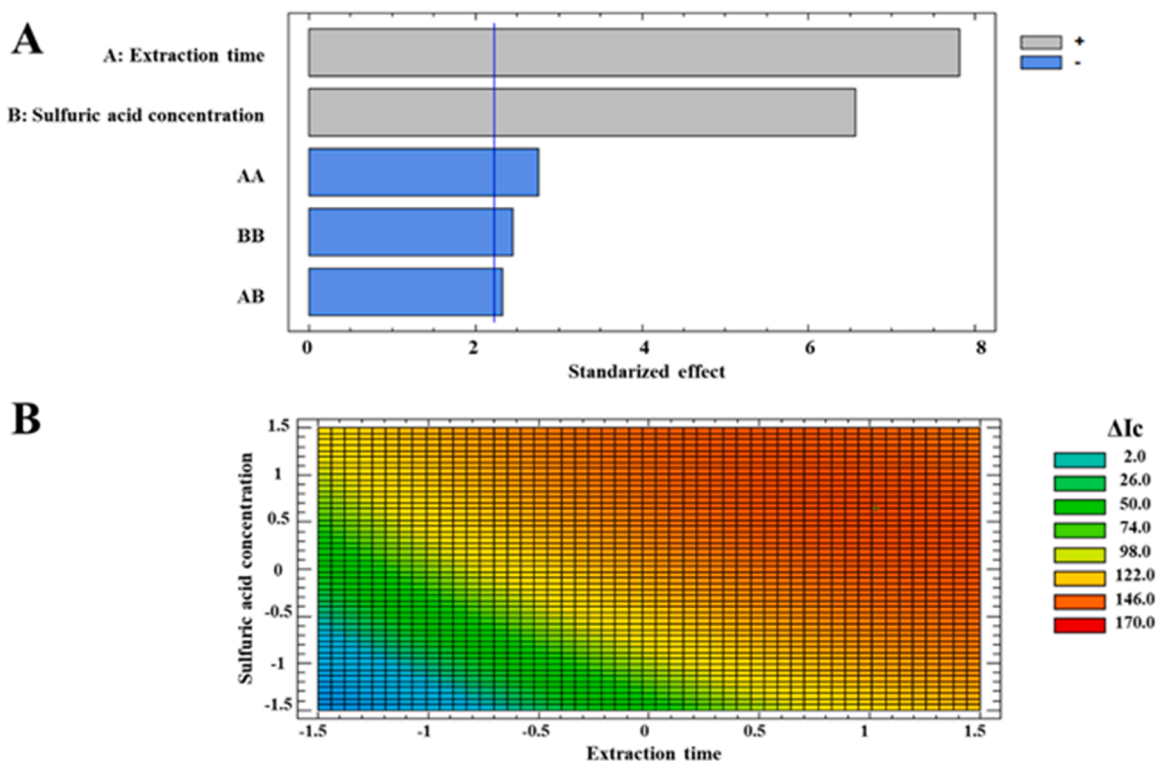


Fig. 3. Pareto chart of the main effects obtained from the CCD (A). Response surface for the CCD between extraction time and sulfuric acid concentration (B).

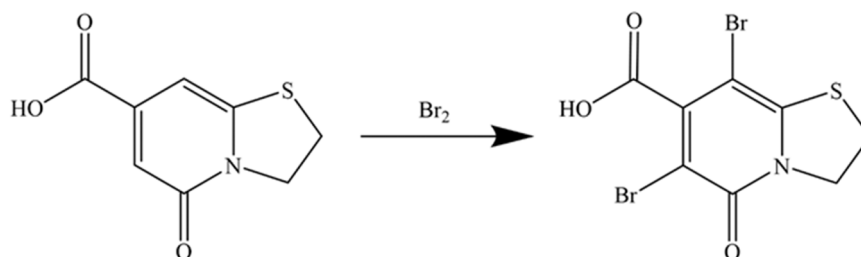


Fig. 4. Chemical reaction of TPCA with bromine.

### 3.4. Evaluation of potential interferences

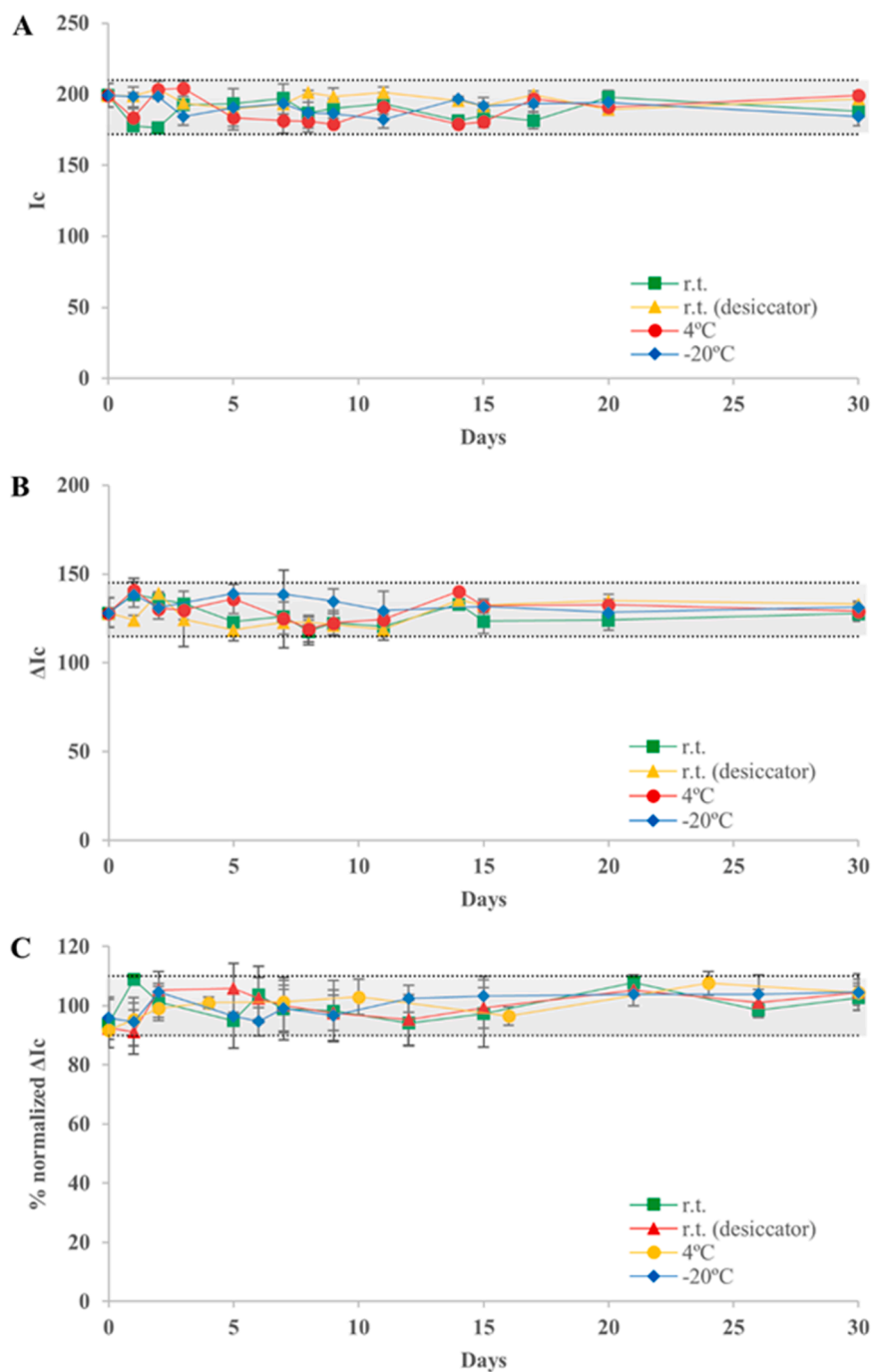
The effect of potential interferences on the analytical response was evaluated. Interference effects were considered when the analytical response of blanks and standards varied beyond  $\pm 10\%$  in the presence of potential interferences. No interference effects were found in the presence of  $500,000 \mu\text{g L}^{-1}$  carbonate,  $100,000 \mu\text{g L}^{-1}$  iodate, chloride, hypochlorite, sodium and potassium,  $1000 \mu\text{g L}^{-1}$  sulfate,  $100 \mu\text{g L}^{-1}$  phosphate and nitrate, and  $10 \mu\text{g L}^{-1}$  humic acid. Furthermore, metal ions, including Cu(II), Fe(III) and Zn(II), did not cause any significant variation on the analytical signal at a  $100,000 \mu\text{g L}^{-1}$  concentration level.

### 4. Analytical performance

The analytical characteristics of the proposed method were evaluated under optimal conditions. The calibration curves for  $\text{Br}^-$  and  $\text{BrO}_3^-$  (Fig. 6), were linear in the ranges of  $30\text{--}150 \mu\text{g L}^{-1}$  and  $5\text{--}25 \mu\text{g L}^{-1}$ , respectively, with regression coefficients of 0.9966 and 0.9976, respectively. The limits of detection (LODs) and quantification (LOQs), calculated according to the  $3\sigma$  and  $10\sigma$  criteria, respectively, were  $5.4 \mu\text{g L}^{-1}$  and  $17.9 \mu\text{g L}^{-1}$  for  $\text{Br}^-$  and  $0.9 \mu\text{g L}^{-1}$  and  $3.1 \mu\text{g L}^{-1}$  for  $\text{BrO}_3^-$ . The repeatability, expressed as relative standard deviation (RSD), was

determined at two concentration levels by carrying out eight consecutive extractions of aqueous solutions spiked with 30 and  $100 \mu\text{g L}^{-1}$   $\text{Br}^-$  and 5 and  $15 \mu\text{g L}^{-1}$   $\text{BrO}_3^-$  and found to be 7.8% and 8.3% for  $\text{Br}^-$  and 10% and 6.3% for  $\text{BrO}_3^-$ , respectively.

A comparison of the proposed method with non-instrumental approaches reported in the literature for determination of  $\text{Br}^-$  and/or  $\text{BrO}_3^-$  is provided in Table 1. It can be inferred from the Table that the proposed method shows comparable or improved LODs for determination of bromine species and acceptable repeatability. The analysis time is comparable to that of other assays involving enrichment [24,27,28,53] but higher than that of direct assays [54,55]. Nevertheless, several samples can be processed simultaneously, thus achieving an excellent sample throughput. Regarding the fastest approaches [54,55], the flow through assay [54] shows excellent portability and sample throughput, but its LOD is not sufficiently low for the determination of  $\text{Br}^-$  at environmentally-relevant concentration levels, whereas the fluoroionophore pyrene-linked calix[4]arene [55] shows excellent sensitivity not only toward  $\text{Br}^-$ , but also toward As(III) and Nd(III), these species thus being potential interferences for the determination of the halide. Both assays are aimed at detecting a single bromine species. On the other hand, unlike in other assays where commercially available reagents are used for sensing purposes [53,54], the recognition element used in this work, *i.e.*, TPCA, is not commercially available but easily



**Fig. 5.** Effect of storage conditions on the analytical response. Mean color intensity of PADS stored under four different conditions (A). Analytical response of PADS exposed to bromine vapor after being stored under different conditions (B). Analytical response of PADS stored under different conditions after being exposed to vapor bromine (C).

prepared from natural compounds without involving organic solvents. In conclusion, the reported method enables the sensitive determination of both bromine species, is straightforward and cost-effective, and PADS show excellent stability.

It is worth noting that the proposed approach was optimized with the stringent aim of reaching sufficient sensitivity for its application to the determination of bromine species in environmental samples in agreement with the WHO guidelines. Even though the approach could be used for on-site analysis, some strategies can be identified to minimize or avoid technical requirements, thus making the approach more flexible and amenable for this purpose. For instance, a range of battery-powered portable magnetic stir plates and battery-operated UV lamps are

commercially available and can be used for field analysis in agreement with the procedure described in Section 2.6. Alternatively, the use of a UV-LED as emitter in combination with the smartphone camera [56] represents an attractive alternative to the use of a handheld UV lamp that would be applicable with the TPCA-modified PADS reported herein. In addition, PADS can be exposed to blanks, standards and samples processed simultaneously without agitation and, after a prescribed time, digitized for quantitative analysis. Equivalent performance would be achieved even under non-equilibrium conditions without the requirement to perform agitation, although extended analysis times would be required in this case. This option could also be considered to perform the enrichment step during transportation followed by PADS digitization

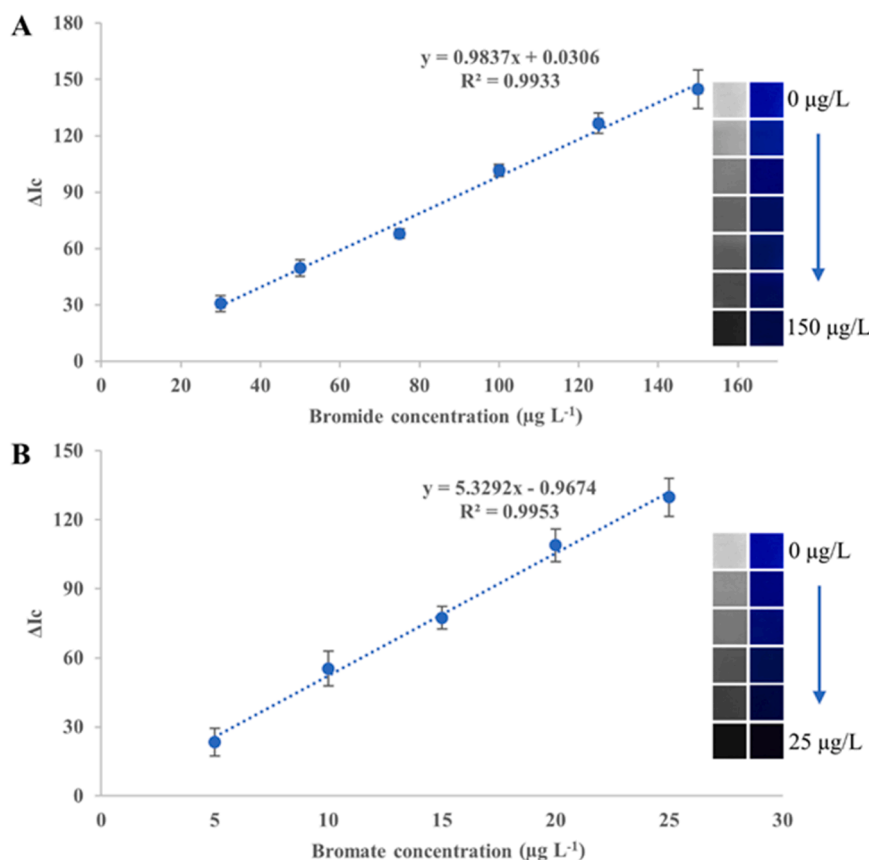


Fig. 6. Calibration graphs for  $\text{Br}^-$  (A) and  $\text{BrO}_3^-$  (B). The inset of each figure shows digital photographs of the detection areas of TPCA-containing PADs (under UV lamp) exposed to increasing concentrations of vapor bromine.

Table 1

Comparison of non-instrumental methods involving PADs and optical detection for  $\text{Br}^-$  and/or  $\text{BrO}_3^-$  determination.

Bromine species	Recognition element	Commercial availability of recognition element	LOD ( $\mu\text{g L}^{-1}$ )	Working range ( $\mu\text{g L}^{-1}$ )	Repeatability (RSD)	Analysis time (min)	References
$\text{Br}^-$	Phenol red and chloramine T	Yes	3218	LOD-10000	–	<1	[54]
$\text{Br}^-$	Pyrene-linked calix[4]arene	No	0.9	0.08–9.6	–	5	[55]
$\text{Br}^-$	Methyl orange	Yes	40	–	5–6%	20	[53]
$\text{Br}^-$	Silver triangular nanoparticles	No	20	50–1500	2.1–4.1%	20	[27]
$\text{Br}^-$	Silver triangular nanoplates	No	20	–	6.0%	20	[28]
$\text{Br}^-$ and $\text{BrO}_3^-$	Silver nanoprisms	No	10	25–2000	–	15	[24]
$\text{Br}^-$ and $\text{BrO}_3^-$	TPCA	No	5.4 0.9	30–1505–30	8.3% 6.3%	30	This work

upon arrival to the laboratory, in a similar fashion to the recently introduced ‘in-transit sample preparation’ concept [57].

Finally, the method was validated against two certified reference materials (CRMs), namely BCR-611 (groundwater, certified concentration of  $\text{Br}^-$ :  $93 \pm 4 \mu\text{g kg}^{-1}$ ) and BCR-612 (groundwater, certified concentration of  $\text{Br}^-$ :  $252 \pm 10 \mu\text{g kg}^{-1}$ ). No significant differences were observed between the found concentration for BCR-611 ( $93 \pm 4 \mu\text{g kg}^{-1}$ ,  $n = 4$ ) and BCR-612 ( $249 \pm 8 \mu\text{g kg}^{-1}$ ,  $n = 4$ ) and the certified concentration values ( $t_{\text{exp}} < t_{\text{crit}}$ ) (Table 2).  $\text{BrO}_3^-$  contents were also determined in these CRMs by the proposed method (Table 2) and found in agreement with the expected  $\text{BrO}_3^-$  levels bearing in mind the total bromine content provided as indicative values in both CRMs ( $107 \mu\text{g kg}^{-1}$  in BCR-611 and  $277 \mu\text{g kg}^{-1}$  in BCR-612, respectively).

Furthermore, the method was applied to the analysis of

environmental aqueous samples of different complexity, the obtained results being shown in Table 2. Suitable dilution of sea water samples was required for  $\text{Br}^-$  determination due to the relatively high concentration levels of the halide in these samples. As can be observed,  $\text{Br}^-$  concentrations of  $72 \pm 3 \text{ mg L}^{-1}$  and  $75 \pm 6 \text{ mg L}^{-1}$  were found in sea water samples, whereas  $\text{BrO}_3^-$  was not detected. Recovery studies were carried out by spiking water samples and found in the ranges of 93–101% and 97–106% for  $\text{Br}^-$  and  $\text{BrO}_3^-$ , respectively (Table 2). The above results demonstrate the suitability of the proposed non-instrumental method for the straightforward detection of bromine species in environmental water samples.

**Table 2**Analytical results for the determination of Br<sup>-</sup> and BrO<sub>3</sub><sup>-</sup> in water samples.

Samples	Added Br <sup>-</sup> concentration (µg L <sup>-1</sup> )	Found Br <sup>-</sup> concentration (µg L <sup>-1</sup> )	Recovery (%)	Added BrO <sub>3</sub> <sup>-</sup> concentration (µg L <sup>-1</sup> )	Found BrO <sub>3</sub> <sup>-</sup> concentration (µg L <sup>-1</sup> )	Recovery (%)
BCR-611	–	93 ± 4 µg L <sup>-1a</sup>	–	–	17.6 ± 1.2 µg L <sup>-1</sup>	–
BCR-612	–	249 ± 8 µg L <sup>-1b</sup>	–	–	22.2 ± 0.7 µg L <sup>-1</sup>	–
Sea water (Samil)	–	72 ± 3 mg L <sup>-1c</sup>	–	–	<LOD <sup>c</sup>	–
Sea water (O Vao)	–	75 ± 6 mg L <sup>-1c</sup>	–	–	<LOD <sup>c</sup>	–
River water	100	98 ± 8 µg L <sup>-1</sup>	98 ± 8	15	15.9 ± 0.6 µg L <sup>-1</sup>	106 ± 4
Drinking water	100	101 ± 7 µg L <sup>-1</sup>	101 ± 7	15	14.7 ± 1.2 µg L <sup>-1</sup>	98 ± 8
Fountain water	100	93 ± 6 µg L <sup>-1</sup>	93 ± 6	15	14.5 ± 1.1 µg L <sup>-1</sup>	97 ± 8

<sup>a</sup>  $t_{exp}$  is 0.7952 and  $t_{crit}$  is 3.18 ( $\alpha$  0.05, 2 tails).<sup>b</sup>  $t_{exp}$  is 0.0005 and  $t_{crit}$  is 3.18 ( $\alpha$  0.05, 2 tails).<sup>c</sup> Results obtained by the standard addition method.

## 5. Conclusions

This work reports on the development of an inexpensive, sensitive and straightforward non-instrumental method for bromine speciation analysis involving TPCA, a luminescent probe derived from natural compounds. The method entails *in situ* bromine generation, its simultaneous trapping and reaction at the detection area of a TPCA-containing PAD, and smartphone-based detection. TPCA-modified PADs are easily prepared and, unlike alternative approaches, show excellent stability under a wide range of storage conditions. The luminescence quenching of TPCA observed in the presence of bromine was attributed to the formation of a stable dibrominated derivative of the probe in the detection area of the PAD. This fact, together with the high stability of TPCA-modified PADs, provides high flexibility for their applicability. The method allows the determination of bromine species in waters at concentration levels well below the guideline values set by the WHO for both anions.

## CRediT authorship contribution statement

**Lorena Placer:** Formal analysis, Resources, Data curation, Visualization. **Isela Lavilla:** Data curation, Resources, Supervision, Validation. **Francisco Pena-Pereira:** Conceptualization, Methodology, Writing – original draft, Supervision. **Carlos Bendicho:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition.

## 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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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.snb.2022.131499](https://doi.org/10.1016/j.snb.2022.131499).

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