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A paper-based colorimetric assay with non-instrumental detection for determination of boron in water samples

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Abstract

The present work reports on the combination of paper-based analytical devices (PADs) and information technology (IT) equipment for non-instrumental determination of boron. PADs prepared with curcumin as a receptor and ethanolic extracts of *Curcuma longa* L. powder were evaluated for sensing. The colorimetric assay is based on a two step-strategy involving initially the formation of rosocyanin in the PAD under acidic conditions, with subsequent color change (from red to blue-green) at alkaline pH. The color change produced in the PAD is then exploited for determination of boron by digitization and image processing with IT devices (scanner and tablet camera) and an image analysis program, respectively. Under optimal conditions, the proposed assay showed limits of detection in the range 0.2 to 0.8 mg/L depending on the PADs and IT devices used for colorimetric reaction and digitization, respectively. In addition, the repeatability, expressed as relative standard deviation, was found to be below 5% (5 mg/L, N=10). PADs prepared with curcumin and ethanolic extracts of *Curcuma longa* L. powder showed excellent lifetime and successful applicability to the analysis of water samples of different complexity with recoveries in the range 93 to 105%.

Keywords

Boron; curcumin; paper-based device; colorimetric assay; non-instrumental detection; water analysis

1. Introduction

Paper-based spot tests have been widely used in classical qualitative analysis for identification of target analytes. Recently, the combination of paper-based analytical devices (PADs) with everyday information technology (IT) and communications devices has opened up new opportunities in the analytical field [1]. Thus, this combined approach has enabled the development of simple, rapid and affordable analytical methods for point-of-care and on-site analysis [2–5]. PADs make use of cellulose substrates as advantageous detection platforms due to their high porosity, compatibility with a wide range of reagents and low cost. PADs are used with a number of detection techniques among which colorimetric detection is especially convenient due to its simplicity and applicability with portable digitization devices [6,7]. In fact, the color change produced by interaction/reaction of the target analyte with the recognizing element present in the PAD can be monitored by means of scanners, digital cameras and smartphones in combination with image processing programs, thus showing potential for low-cost field analysis.

Boron is an essential micronutrient for humans. However, excess or deficiency of boron adversely affects reproductive function of living organisms as well as the development of crops and plants [8,9]. Natural boron input sources to the environment include mainly volcanic activity and rock/soil weathering, whereas mining, biomass burning and fossil fuel combustion are considered the main anthropogenically-derived

boron sources [10]. Boron is also used in glass production and present in detergents and fertilizers, thus contributing to increased boron concentration in wastewaters which could reach surface waters. Boron monitoring in water samples is of paramount importance in several fields, including marine biochemistry, geochemistry, environmental sciences, hydrology, desalination and even nuclear technology [8]. The determination of boron in waters is generally carried out by means of inductively coupled plasma-optical emission spectrometry (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS), spectrofluorimetry and UV-vis spectrophotometry [11,12]. ICP-OES and ICP-MS allow multielemental determination, even though they are costly, prone to interferences, and require expert personnel [11,12]. A number of spectrofluorimetric methods have been reported [13,14], although spectrophotometric methods are more commonly employed. A variety of colorimetric reagents have been used with this aim, including azomethine-H [15], carminic acid [12,16,17], or curcumin [12,18,19], among others. Particularly, curcumin, a major component of the Indian spice and medicinal plant *Curcuma longa* L. (commonly known as turmeric), has been recommended for the qualitative identification and determination of boron on the basis of the colorimetric reaction produced [18,19]. Colorimetric methods involving curcumin are usually based on the formation of rosocyanin, a 1:2 spiroborate ester of the natural antioxidant present in *Curcuma longa* L. [18,19]. The implementation of natural compounds in analytical methods has been identified as a challenging aspect in terms of green analytical chemistry (GAC) that has been underexplored so far [20,21]. In particular, the use of *Curcuma longa* L. extracts as acid-base indicator has been reported in the literature [22]. In this vein, the use of extracts of *Curcuma longa* L. for boron determination could be of relevance from a GAC perspective.

This work reports for the first time on the development of a paper-based assay with non-instrumental detection for the colorimetric determination of boron in complex water samples. Specifically, a classical curcumin-based colorimetric reaction for qualitative identification of boron is revisited in combination with everyday communications and information technologies to turn a qualitative spot test into a quantitative non-instrumental colorimetric assay. In addition, the use of unrefined extracts of *Curcuma longa* L. for the colorimetric determination of boron has also been considered.

2. Experimental

2.1.Reagents, materials and apparatus

A Milli-Q RG ultrapure water system (Millipore, Molsheim, France) was used to produce high purity water of 18.3 MΩ cm resistivity. All chemicals were of analytical reagent grade. Stock solutions of boron were prepared from $B(OH)_3$ (Prolabo, Paris, France). Working standard solutions were prepared daily by appropriate dilution of stock solutions. Matrix-matched standards used to analyze seawater samples were prepared by spiking known amounts of boron into boron-free artificial seawater ASTM D1141-98 [23]. Curcumin (Acros Organics, New Jersey, USA), *Curcuma longa* L. powder (La Colmena, Novelda, Spain) and ethanol (VWR Chemicals, Fontenay-sous-Bois, France) were used to prepare PADs. Hydrochloric acid 37% and sodium hydroxide (VWR Prolabo) were used for the colorimetric determination of boron. The following chemicals were used for evaluating potential interferences and/or preparation of synthetic water samples: iron(III) chloride hexahydrate, manganese sulfate monohydrate, potassium bromide and ammonium molybdate from Sigma-Aldrich (St. Louis, MO, USA); copper chloride dihydrate, strontium nitrate, sodium fluoride and ammonium dihydrogen phosphate from Merck (Darmstadt, Germany); magnesium

chloride hexahydrate, sodium nitrite, sodium phosphate tribasic dodecahydrate and glucose L-hydrate from Panreac (Barcelona, Spain); sodium nitrate, nickel chloride hexahydrate, zinc sulfate and ammonium nitrate from Probus (Badalona, Spain); sodium chloride and humic acid from Flucka Chemie (Buchs, Switzerland); potassium chloride and potassium dichromate from Prolabo; sodium sulfate and sodium bicarbonate from Carlo Erba (Milan, Italy); cobalt chloride hexahydrate from Scharlau (Barcelona, Spain); and calcium chloride dihydrate from Fisher scientific (Pittsburgh, PA, USA). Oxalic acid dihydrate (Merck) was also used for preparation of the curcumin reagent used in the 4500-B B standard method [12].

Whatman No. 1 and No. 3 filter papers obtained from Whatman (Maidstone, Kent, UK) were evaluated as paper substrates. A hair dryer was used to ensure rosocyanin formation in the PAD by water removal. Digitization of PADs was carried out with a Canon PIXMA MG3650 desktop scanner (Tokio, Japan) or, alternatively, a tablet equipped with an 8-megapixel rear camera (Samsung Galaxy Tab S2, Seoul, South Korea). ImageJ [24], a free image processing and analysis software, was used for data acquisition.

An Agilent Cary 300 UV-vis spectrophotometer (Agilent Technologies, Palo Alto, USA) was used for determination of boron in water samples in accordance with the 4500-B B method [12].

2.2.*Preparation of PADs*

PADs containing curcumin were prepared by immersing a Whatman No. 1 substrate (150 mm diameter) in a 50 mL of ethanolic solution of curcumin (1 mg/mL) for 1 h protected from the light. Then, the modified substrate was allowed to dry at 50 °C and stored in a desiccator protected from the light with aluminum foil prior to use.

An analogous procedure was used to prepare PADs modified with ethanolic extracts of *Curcuma longa* L. In this case, curcumin was extracted from powdered *Curcuma longa* L. as described elsewhere [25]. In brief, turmeric powder was extracted with ethanol for 30 min under vigorous agitation at 60 °C. Subsequently, a Whatman No. 1 substrate was immersed into the ethanolic extract (50 mL) for 3 h protected from the light. Then, the modified substrate was allowed to dry at 50 °C and stored in a desiccator protected from light prior to use.

2.3.*Experimental procedure*

A schematic representation of the experimental procedure is shown in **Fig. 1**. A 2 μL volume of aqueous solution (blank, standard or sample) containing HCl 1 M was spotted onto the PAD and the spot dried with a hair dryer until a homogeneous color change was noticeable (10 s). Subsequently, 4 μL of NaOH 1 M was deposited over the colored spot. After 10 s, the PAD was digitized (by means of a scanner or a tablet camera) and processed with ImageJ. In particular, the image was inverted and the mean color intensity in the red channel of the RGB color space was obtained.

2.4.4500-B B. Curcumin method procedure [12]

A volume of up to 1 mL of blank, standards and samples and 4.0 mL of a curcumin reagent (curcumin 0.04% (m/v), oxalic acid 5.0% (m/v), HCl 4.2% (v/v) and ethanol 95% (v/v)) was pipetted into evaporating dishes. After gently mixing the contents, the evaporating dishes were floated on a water bath at 55 °C for 80 min. Once the dishes reach room temperature, the resulting colored product was dissolved with ethanol 95% (v/v) and wash contents transferred to 25-mL volumetric flasks, using ethanol 95%

(v/v). The final solutions were filtered if needed, and absorbance measurements were performed at 540 nm.

3. Results and discussion

3.1. Fundamentals of the method

The chemical reactions involved in the present method are shown in **Fig. 2**. The paper-based colorimetric assay involves a chemical reaction between boric acid and curcumin to yield rosocyanin, a cationic 2:1 complex in which the boron atom is tetrahedrally coordinated by two curcumin molecules [26,27]. The formation of rosocyanin proceeds by formation of a reactive form of curcumin in acidic media and absence of water [28]. At least one of the curcumin molecules involved in the reaction should be present in the diol form to condense with the hydroxyl groups of boric acid. Once formed, the color of rosocyanin changes from red (at acidic pH) to blue-green in alkaline media due to the structural change from benzenoid to quinoid structures [26]. The corresponding color change remarkably enhances the selectivity of the assay [18]. A careful control of analysis time is, however, mandatory since the alkaline media catalyzes the conversion of formed rosocyanin into $B(OH)_4^-$ and curcumin [26].

3.2.Evaluation of experimental parameters

3.2.1. Color mode detection

The selection of color mode detection was initially considered. Ideally, the selected color mode must ensure reduced blank values and high sensitivity in the presence of the analyte. PADs treated with blanks and standard solutions of boron were digitized and the mean color intensity of R, G and B channels was obtained. Alternatively, digital

images were converted into grayscale before obtaining the corresponding mean color intensity. The obtained results are shown in **Fig. 3**. As can be deduced from the figure, the red channel offered the highest sensitivity with reduced blank values. Therefore, the red channel was selected for further studies.

3.2.2. Preparation of PADs

The conditions required for obtaining PADs modified with curcumin and ethanolic extracts of *Curcuma longa* L. powder were also evaluated and the results shown in **Fig. 4**. As can be observed in **Figs. 4A** and **B**, the highest analytical response of boron was achieved by setting the curcumin concentration and impregnation time at least at 0.5 mg/mL and 60 min, respectively, with no further improvements above these values. On the other hand, an extended impregnation time (at least 3 h) was required to achieve the highest analytical response with PADs prepared from ethanolic extracts of *Curcuma longa* L. powder (**Fig. 4B**). These extended impregnation conditions can presumably be attributed to the presence of co-extracted compounds that could hinder the immobilization of curcumin on the solid substrate.

3.2.3. Parameters affecting rosocyanin formation in the solid substrate

The type of cellulose substrate can show a remarkable effect on the analytical response of boron. Thus, two paper substrates with different thickness and porosity, namely Whatman No. 1 and No. 3, have been evaluated for boron determination. The analytical signal obtained with Whatman No. 1 was significantly higher (ca. 20%) than obtained with Whatman No. 3. Thus, Whatman No. 1 was selected as the substrate for further investigations.

As described in *section 3.1*, and shown in **Fig. 2**, acidic media is required for quantitatively generating rosocyanin by reaction of boric acid with curcumin. Thus, the concentration of hydrochloric acid needed to determine boron by the curcumin assay has been assessed. The effect of this variable on the analytical response was evaluated in the range 0.1-2.0 M (**Fig. 5A**). It can be observed in the figure that the analytical signal increased by increasing the HCl concentration up to 1.0 M, whereas the analytical signal remained unchanged for higher concentrations. Besides, higher concentrations of the acid resulted in the formation of a non-homogeneous color product that hindered the quantitative analysis. This effect could be ascribed to the decomposition of curcumin present in the cellulose substrate in highly acidic media [28]. On the basis of these results, the concentration of HCl was set at 1.0 M.

The color of formed rosocyanin highly depends on the pH of the media. Particularly, it is violet-red in acidic media, whereas it shows a blue-green color in alkaline media that dramatically increases the selectivity of the assay for boron determination [18]. As shown in **Fig. 5B**, increasing amounts of NaOH resulted in an enhancement of the analytical response up to a concentration of 1.0 M. A slight decrease of the analytical signal was observed at higher concentration values probably due to the increase in the rate of hydrolysis in highly alkaline media [26]. Thus, 4 µL of 1.0 M NaOH was selected to ensure the conversion of rosocyanin formed in the PAD to its anionic form.

Water removal is required to favor the formation of rosocyanin, as can be deduced from **Fig. 2**. While this requirement makes conventional curcumin-based colorimetric methods be tedious and time-consuming [19], the reduced sample volume used in the proposed assay and the porous nature of the cellulose substrate is expected to solve the issue, then increasing the sample throughput. Thus, drying time was assessed in this work, showing a relevant effect on the analytical signal (**Fig. 5C**). The use of drying

times below 10 s resulted in reduced sensitivity due to the incomplete formation of the colored product, whereas the use of longer drying times gave rise to increasing blank values that resulted in a lower analytical response, presumably due to the acid-induced decomposition of curcumin. A drying time of 10 s was therefore selected for further experiments.

After formation of rosocyanin, a careful control of the measurement time is of paramount importance, as discussed in *section 3.1*. It is apparent from the results of this study (**Fig. 5D**) that the analytical response steadily decreased in the whole evaluated range (10-180 s). This negative effect could be ascribed to the base-catalyzed hydrolysis of rosocyanin thus yielding $B(OH)_4^-$ and curcumin [26]. Therefore, a measurement time of 10 s was selected with both PADs since it ensured high sensitivity, acceptable precision and high sample throughput.

3.2.4. Digitization parameters

It is well known that the amount of light reflected from a test subject that reaches the camera's image sensor shows a paramount role on the image quality. Thus, digitization parameters can be controlled in electronic devices to attain the optimal exposure. For analytical purposes, digitization parameters should be carefully controlled to ensure the highest sensitivity with low blank values. The exposure value, set by simultaneous adjustment of shutter speed and aperture, was assessed in the range -0.5 to +2.0. As can be observed in **Fig. 6**, the increase of the exposure value resulted in a drastic improvement (decrease) of blank values as well in a slight decrease of the analytical response when using the tablet camera for digitization. Thus, selection of exposure values above +1.0 should be considered in order to avoid excessively high blank values.

Accordingly, an exposure value of +1.9 was selected for further studies since it ensured acceptable sensitivity, wider dynamic range and excellent blank values.

3.2.5. Stability of PADs

The stability of PADs prepared with curcumin and ethanolic extracts of *Curcuma longa* L. powder has been evaluated during 6 weeks. PADs were stored at room temperature and protected from the light before analysis. Non-significant differences in the analytical response obtained with both PADs were observed in the evaluated period, showing recoveries above 90% in both cases. Therefore, PADs prepared with curcumin and ethanolic extracts of *Curcuma longa* L. were found to be highly stable, showing a remarkable lifetime for their application to boron determination.

3.3.Selectivity of the assay

The selectivity of the assay to potential interferences was also studied. Evaluated compounds were considered to interfere at a given concentration level when a variation of the analytical signal beyond ±10% was observed. Non-significant effects on the analytical response were observed when 5 mg/L boron solutions were analyzed with curcumin PADs in the presence of 10,000 mg/L Cl^-, PO_4^{3-}, SO_4^{2-}, K^+ and Na^+; 1,000 mg/L HCO_3^-, NO_3^- and Fe^{3+}; 100 mg/L $Cr_2O_7^{2-}$, Mg^{2+}, Cu^{2+} and humic acid; and 10 mg/L NO_2^-. The selectivity of PADs prepared from ethanolic extracts of *Curcuma longa* L. powder was also evaluated, showing similar or slightly lower tolerance to interferences than those obtained with curcumin PADs. Specifically, PADs prepared from ethanolic extracts of *Curcuma longa* L. powder showed lower tolerance to HCO_3^- (100 mg/L), Fe^{3+} (100 mg/L) and $Cr_2O_7^{2-}$ (10 mg/L), whereas equivalent tolerance ratios were observed for the rest of studied compounds.

3.4.Analytical characteristics

The analytical figures of merit were obtained under optimal conditions with PADs prepared with curcumin and *Curcuma longa* L. extracts using two different digitization systems (namely, a scanner and a tablet camera) and summarized in **Table 1**. As expected from previous studies involving PADs [29–31], the analytical response showed a non-linear relationship with the concentration of the analyte (**Fig. 7**). Instead, the curve was better adjusted to a rectangular hyperbolic curve. Thus, the calibration graph could be described by the following equation:

$$I = \frac{I_{max}[B]}{K+[B]} \quad (2)$$

where I is the mean color intensity (analytical response), I_{max} is the maximum achievable signal, K is a constant equal to the concentration of boron at $I_{max}/2$ and $[B]$ is the concentration of boron. Rearranging Equation (2), a linear relationship can be obtained between $K/(I_{max}/I)-1)$ and $[B]$ with ideally unity slope and zero intercept, in such a way that the values of I_{max} and K can be easily obtained with the Excel's Solver Tool (Microsoft 2010) for quantitative purposes. The limits of detection of the assay, calculated at a signal-to-noise ratio of 3, were found to be in the range 0.2-0.8 mg/L, when PADs were digitized with a scanner and a smartphone camera, respectively. In general, lower LODs were obtained with curcumin-based PADs. The corresponding limits of quantification, calculated at a signal-to-noise ratio of 10, were in the range 0.7 to 2.6 mg/L. The repeatability, expressed as relative standard deviation (RSD), was lower than 5% (5 mg/L, N=10) in all cases. In comparison with alternative colorimetric methods reported in the literature for boron determination in water samples (**Table 1**), the proposed paper-based assay shows highly reduced analysis time, slightly lower

sensitivity, acceptable precision and an almost negligible consumption of sample and chemicals per analysis.

3.5.Boron determination in water samples

The colorimetric assay was finally applied to the determination of boron in a number of water samples. The obtained results were compared with those obtained with the reference method [12] and recovery studies were also carried out at two concentration levels to assess the accuracy of the method. The results obtained by applying the assay to the analysis of three wastewater samples, namely a synthetic wastewater sample [32] and two samples collected from the inlet and outlet of the wastewater treatment plant of a paper company, are shown in **Table 2**. Boron was found below the LOD of the proposed assays and the reference method, whereas quantitative recoveries (96-105%) were obtained with both PADs using the external standard method for boron determination in wastewater samples. In addition, seawater samples were analyzed using the proposed assay and the obtained results are shown in **Table 3**. It should be noted that matrix-matched calibration was required in this case, as expected from the results shown in *section 3.3*. Thus, a boron-free synthetic seawater [23] was used for preparation of blanks and standards to alleviate for potential matrix effects. The average concentration levels found in seawater samples were in the range 4.4-5.0 mg/L (**Table 3**), which fall in the typical range of boron concentrations in seawater samples [33]. No significant differences were observed between the proposed colorimetric assays and the reference method (t-test, p 0.05, two tails). As can be observed in the **Table**, quantitative recoveries (93-104%) were obtained in all analyzed seawater samples. The above results demonstrate the practical applicability of the proposed assay to the rapid and simple determination of boron in water samples.

4. Conclusions

The present work reports on the development of a non-instrumental paper-based assay for boron determination in water samples on the basis of the selective colorimetric reaction of the analyte with curcumin-containing substrates. Remarkably, PADs prepared with both the colorimetric reagent (curcumin) or ethanolic extracts of powdered *Curcuma longa* L. were successfully applied to the non-instrumental quantification of boron in wastewater and seawater samples after digitization with both a scanner and a tablet camera. In short, the combination of PADs with everyday communications and IT equipment offers new avenues for the development of rapid and cost-effective quantitative methods for field analysis without using advanced analytical instrumentation.

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Figure captions

Figure 1. Schematic representation of the experimental procedure for boron determination.

Figure 2. Chemical reactions involved in the colorimetric assay.

Figure 3. Effect of color mode detection on the analytical response.

Figure 4. Effect of experimental parameters affecting the preparation of PADs on the analytical response of boron: Concentration of curcumin (A), impregnation time with curcumin and *Curcuma longa* L. extract (B).

Figure 5. Effect of experimental parameters on the analytical response: HCl concentration (A), NaOH concentration (B); drying time (C), measuring time (D).

Figure 6. Effect of the exposure value on the analytical response of boron using a tablet camera for digitization.

Figure 7. Plots of mean color intensity *vs* concentration of boron obtained with curcumin-based PADs (A) and *Curcuma longa* L. extract-based PADs (B) using a scanner (red dots) and a tablet camera (black dots) for digitization.

Table 1

Analytical characteristics of the proposed method and previously reported colorimetric methods for boron determination in waters

Colorimetric reagent	Analytical method	LOD (mg/L)	Repeatability (RSD, %)	Analysis time (min)	Sample volume (mL)	Reference
Carminic acid	Microfluidic ion exchange resin-UV-vis	0.3	4.2	42	2	[17]
Carminic acid	UV-vis	0.01-0.3	2.6-13.7	30	0.2-0.5	[16]
MPVTI	DLLME-UV-vis	0.003	5.6	< 15	1.5	[34]
Azomethine-H	UV-vis	0.02	1.4	60-120	5	[35]
Azomethine-H	Multi-pumping flow analysis-UV-vis	0.1	< 3	6	0.6	[15]
Curcumin	UV-vis	n.r.	< 0.3	105	0.5	[19]
Curcumin	**PAD (scanner)**	**0.3**	**4.0**			
Curcumin	**PAD (tablet)**	**0.4**	**4.0**	**< 1**	**0.002**	**This work**
***Curcuma longa* L. extract**	**PAD (scanner)**	**0.6**	**4.8**			
***Curcuma longa* L. extract**	**PAD (tablet)**	**0.8**	**5.0**			

DLLME, dispersive liquid-liquid microextraction; MPVTI, 2-[2-(4-methoxy-phenylamino)-vinyl]-1,3,3-trimethyl-3H-indolium; UV-vis, ultraviolet-visible spectrophotometry

Table 2

Analytical results obtained in the analysis of wastewater samples

Wastewater samples	**Curcumin-based PADs**			***Curcuma longa* L. extract-based PADs**			**4500 B method**
	Added boron concentration (mg/L)	**Found boron concentration (mg/L)[a]**	**Recovery (%)**	**Added boron concentration (mg/L)**	**Found boron concentration (mg/L)[a]**	**Recovery (%)**	**Found boron concentration (mg/L)[b]**
Synthetic wastewater	--	<LOD	-	--	<LOD	-	<LOD
	2.5	2.49±0.17	100±7	5.0	5.13±0.05	103±1	
	5.0	5.13±0.18	103±4	10.0	10.2±0.6	102±6	
Pulp wastewater (inlet)	--	<LOD	-	--	<LOD	-	<LOD
	2.5	2.56±0.15	102±6	5.0	5.22±0.24	104±5	
	5.0	5.2±0.3	105±5	10.0	10.1±0.4	101±4	
Pulp wastewater (outlet)	--	<LOD	-	--	<LOD	-	<LOD
	2.5	2.42±0.16	96±6	5.0	5.12±0.14	102±3	
	5.0	5.1±0.3	102±5	10.0	9.8±0.5	98±5	

[a]Results obtained by external calibration, N=4.

[b]Results obtained by external calibration, N=3.

Table 3

Analytical results obtained in the analysis of seawater samples

Seawater samples	**Curcumin-based PADs**			***Curcuma longa* L. extract-based PADs**			**4500 B method**
	Added boron concentration (mg/L)	**Found boron concentration (mg/L)[a]**	**Recovery (%)**	**Added boron concentration (mg/L)**	**Found boron concentration (mg/L)[a]**	**Recovery (%)**	**Found boron concentration (mg/L)[b]**
Samil (Vigo)	--	4.76±0.20	-	--	4.4±0.9	-	4.69±0.22
	2.5	7.21±0.08	97.7±1.1	5.0	9.5±1.2	101±13	
	5.0	9.5±0.5	95±5	10.0	13.7±0.9	93±6	
Baltar (Sanxenxo)	--	4.95±0.13	-	--	4.7±0.5	-	4.87±0.29
	2.5	7.43±0.25	99±3	5.0	9.5±1.1	96±11	
	5.0	9.9±0.4	99±4	10.0	14.6±1.7	99±12	
Areagrande (O Grove)	--	4.59±0.22	--	--	4.7±0.9	-	4.43±0.43
	2.5	7.02±0.25	97±3	5.0	9.8±1.1	103±12	
	5.0	9.8±0.4	104±4	10.0	14.2±1.7	96±12	

[a]Results obtained by matrix-matched calibration, N=4.

[b]Results obtained by external calibration, N=3.