# Point-of-use Determination of Fluoride and Phosphorus in Water through a Smartphone using the PhotoMetrix® App

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Graphical Abstract
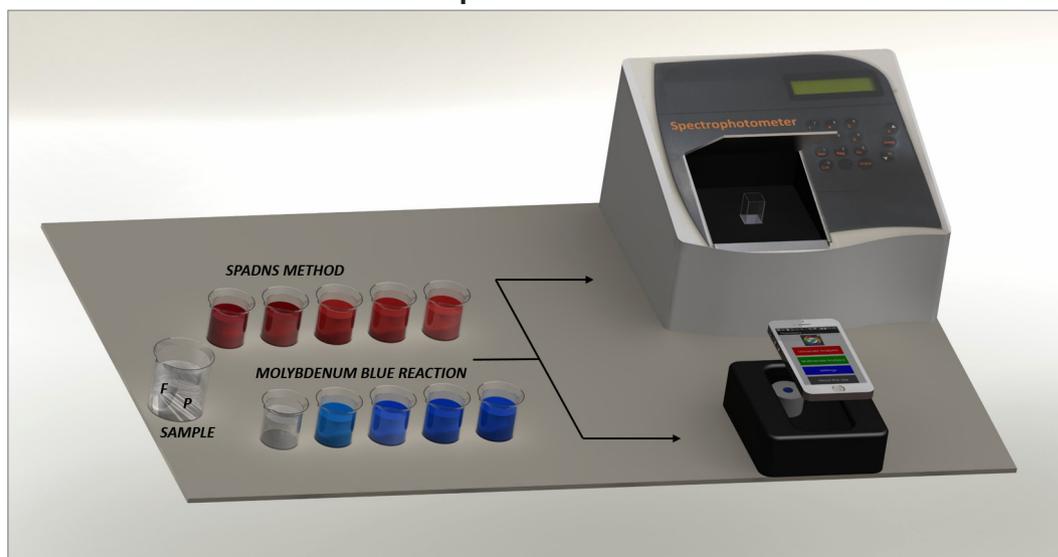
The PhotoMetrix® application was used as a colorimetric analysis tool to determinate the fluoride and phosphorus ion concentration in treated and natural waters.

This research aimed to demonstrate the use of a colorimetric analysis tool using a smartphone application called PhotoMetrix® to determinate the fluoride and phosphorus ion concentration in treated and natural waters. The determinations were made using the conventional spectrophotometric approach [2-(4-sulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate (SPADNS) reagent for fluoride measurements and the molybdenum blue reaction for phosphorus measurements], and then a smartphone equipped with the PhotoMetrix® application was used to compare the results obtained by the two procedures. An analytical curve was developed, and three triplicate samples were analyzed. The coefficient of determination (R^2) for phosphorus and fluoride for the conventional method and for the method using the PhotoMetrix® application were 0.990 and 0.998, and 0.999 and 0.999, respectively. The average results obtained using the application showed satisfactory correspondence values of 99.2% (phosphorus) and 100% (fluoride) compared to the reference method. No significant differences between the two methods of quantification were identified ($p > 0.05$, paired *t*-test). In conclusion, the results demonstrated the efficiency of this new analytical tool, which allows for quick and accurate analysis of fluoride and phosphorus ion concentrations in the field, as well as on an industrial scale.

Keywords: smartphone, water analysis, fluoride, phosphorus, point-of-use

INTRODUCTION

Safe drinking water, whether treated or from a natural source, as defined by the World Health Organization (WHO), should not represent any significant risk to health throughout life, regardless of the

consumer's level of sensitivity [1]. Consequently, the microbiological, physical, and chemical parameters of drinking water must meet certain standards [2,3]. Globally, due to violations of the recommended standards of potable water, around 1.1 billion people lack access to safe drinking water [1,4–6].

The analysis of water quality is extremely important because it enables the detection of various substances, such as fluoride and phosphorus ions [7,8]. The determination of these parameters is usually performed by colorimetric methods commonly applied in the investigation of chemicals in treated waters. Such procedures replace the subjective color responses with an objective numerical system, which allows for the quantification of substances present in the analyzed samples [9].

As established by the regulatory bodies for drinking water, a maximum concentration of 1.5 mg L^{-1} of fluoride is permitted [1]. The presence of this ion in drinking water at controlled levels is important for human health because it prevents cavities. However, excessive ingestion of this substance may cause dental fluorosis, increase the incidence of bone fractures, and impair thyroid function [1,10]. Fluoride can be determined using several methods, such as ion chromatography, gas chromatography, electrochemical procedures, spectrometric measurements, and fluorescence [11–16]. One of the most widely used methods for the determination of fluoride is the 2-(4-sulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate (SPADNS) spectrophotometric method. However, a spectrophotometer is required for the absorbance measurements, and the analysis is not yet suitable for in situ monitoring [17].

In addition to fluoride, phosphorus analysis is also of extreme relevance because, at elevated levels, phosphorous leads to eutrophication and the occurrence of harmful algal blooms [18]. One example is the occurrence of toxic cyanobacterial blooms in surface water supplies [19]. According to Brazilian legislation, a maximum concentration of 0.15 mg L^{-1} of phosphorus is allowed in a lotic environment and in tributaries of intermediate environments [20].

In natural waters, phosphorus can be found in various "dissolved" forms, mostly as inorganic orthophosphates, condensed or polyphosphates, and organic phosphates. Among the most widely used methods for the determination of phosphorus in natural waters is the molybdenum blue reaction. In this reaction, detection is based on the measurement of molybdenum orthophosphate (PO_4^{3-}), using either a batch or flow-based approach. Although, inductively coupled plasma (ICP)-based methods (ICP-atomic emission spectrometry and ICP-mass spectrometry) can also be used if the concentration of phosphorous is sufficiently high [21,22]. However, this equipment is relatively expensive, has limited portability, and requires trained operators.

Thus, it is worthwhile to develop new techniques for water quality determination that provide rapid, low-cost, and portable analytics. Point-of-use technologies have affordable testing systems that bypass the necessity for specialized personnel. Furthermore, such devices can perform analytical measurements in resource-limited environments (e.g., emergency situations), which is a key advantage compared to conventional benchtop approaches [23]. Some smartphone-based colorimetric assays already exist. For example, in the determination of ochratoxin A and microorganisms, viscosity analysis and measurement of fat in cured meat products [24–31]. Moreover, there are currently free applications (apps) available that can be used to make simple and quick calibration curves. Among these methods is the app called PhotoMetrix®, which allows for image acquisition, processing, and presentation of results. This app uses the device's main camera to acquire images, which are analyzed and decomposed by punctuations and uploads [24,32]. The smartphone´s camera functions as a portable colorimeter, allowing for accurate tests to be performed economically in the field (in situ) measurements [25]. The app is able to conduct univariate linear regression calibration with variables separated from the red, green, and blue (RGB); hue, saturation, and value (HSV); hue, saturation, and intensity (HSI); and hue, saturation, and lightness (HSL) color systems. The camera of the smartphone responds to red, green, and blue lights, and it can also perform multivariate calibration [32].

The objective of this study was to develop an analytical methodology for the determination of fluoride and phosphorus ions present in natural waters by monitoring the colorimetric reactions involved in conventional methods through a smartphone based PhotoMetrix® app.

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MATERIALS AND METHODS
Samples, reagents, and standards

The samples were collected from March to July 2017 at the University of Santa Cruz do Sul, RS, Brazil. Three different samples were monitored, one subterranean water (artesian well) sample and two samples of water treated with a bone charcoal filter.

For the determination of fluoride using the SPADNS technique [33], SPADNS reagent (Synth, Diadema, SP, Brazil), zirconium octahydrate ($ZrOCl_2.8H_2O$) (Vetec, Duque de Caxias, RJ, Brazil), HCl (Synth, Diadema, SP, Brazil), and NaF (Synth, Diadema, SP, Brazil) were used.

The SPADNS solution was prepared by dissolving 958 mg of the reagent in 500 mL of deionized water. For the preparation of the zirconium oxychloride solution, 133 mg of the reagent was diluted to 500 mL in a volumetric flask containing 25 mL of distilled water and 350 mL of concentrated HCl. Finally, the colorimetric solution was prepared by mixing equal volumes of SPADNS and zirconium oxychloride solutions.

The determination of aqueous phosphate through the reduction of phosphomolybdic acid using ascorbic acid was conducted, using sulfuric acid (18.4 M, H_2SO_4, Synth, Diadema, SP, Brazil), antimony and potassium tartrate solution [40 g L^{-1}, $K(SbO)C_4H_4O_6 \cdot 1/2H_2O$, Vetec, Duque de Caxias, RJ, Brazil], ammonium molybdate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, Vetec, Duque de Caxias, RJ, Brazil], ascorbic acid (0.1 M, $C_6H_8O_6$, Nuclear, Diadema, SP, Brazil), and trisodium phosphate (Na_3PO_4, Synth, Diadema, SP, Brazil).

A combined reagent was made by mixing 50 mL of sulfuric acid, 5 mL of the antimony and potassium tartrate solution, 15 mL of the ammonium molybdate solution, and 30 mL of the ascorbic acid solution.

Dilutions and reagent preparation were done using distilled and deionized water (>19 MΩ cm^{-1}).

Instrumentation

The conventional colorimetric reactions were performed using a spectrophotometer [33] (Femto, 600 Plus, São Paulo, Brazil).

A Samsung Nexus 5 mobile device, with an Android 6.0.1 operating system, and the PhotoMetrix® app were used. The Photometrix® univariate analysis module was used to perform the calibration and sampling, according to work by Helfer (2017) [24].

The apparatus constructed to analyze the amount of fluoride and phosphorus in the samples through the mobile platform is shown in Figure 1. It consisted of a black, high-density polyethylene box, 42 × 19 × 9 cm in size, with a cover containing an opening for engaging the mobile device. A piece of polytetrafluoroethylene (PTFE, 10 cm in height) was placed in the interior of the box. The piece of PTFE had a central diameter of 1 cm for the addition of the solution and a 0.5 cm diameter in the lateral region for the introduction of a 6 W light emitting diode (LED) lamp. The LED was connected to a device that modulated the power intensity supplied from the battery (9 V) in order to control the intensity of light emitted. The smartphone was positioned on top of the box, and the images were acquired by the main camera (8 megapixel) through the hole in the cover. The luminosity inside the box was maintained with the LED lamp to keep the luminosity variation constant, avoiding the influence of external light.
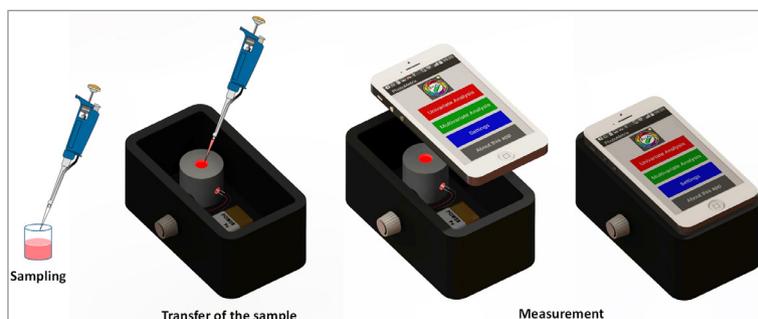
Figure 1. Apparatus used for the analysis with PhotoMetrix®.

Determination of fluoride and phosphorus

The determination of fluoride and phosphorus was performed according to the procedures described in the standard methods for the examination of water and wastewater [33]. A calibration curve was constructed from reference solutions of fluoride in the concentration range 0–1.4 mg L^{-1}. After the addition of the SPADNS reagent and zirconium oxychloride (1 mL) in the samples and in the reference solution (5 mL), the color generated in the reaction was measured after 5 min of equilibration time (but no more than 20 min).

For the determination of phosphorus, a calibration curve was prepared from a phosphate reference standard at concentrations of 0 to 0.25 mg L^{-1}. After the addition of the combined reagent (8 mL) in the samples and in the reference solution (50 mL), the color generated in the reaction was measured after 10 min (but no more than 30 min).

The calibration curves and the samples were analyzed by the conventional method (spectrophotometry at a wavelength of 570 and 580 nm for phosphorus and fluoride, respectively) and by the proposed method.

The region of interest (ROI) in the images acquired by the smartphone camera were 64 × 64 pixels (4096 points of color). The univariate analysis module was used (Figure 2) because the procedures adopted in both analyses were related only to one coloration at different intensities with RGB color system variables.

All samples were analyzed in triplicate. Before the determination of the analytes by the new method, preliminary tests were done to define the optimal distance between the camera and the solution (i.e., the best LED intensity). Fluoride and phosphorus values were expressed in mg L^{-1}.

The figures of merit, such as the accuracy, limit of detection (LOD), and limit of quantification (LOQ), were calculated according to the EURACHEM manual (2014). Estimation of the LOD (3s) and LOQ (10s) was done by considering the analysis of 10 blank samples [34].

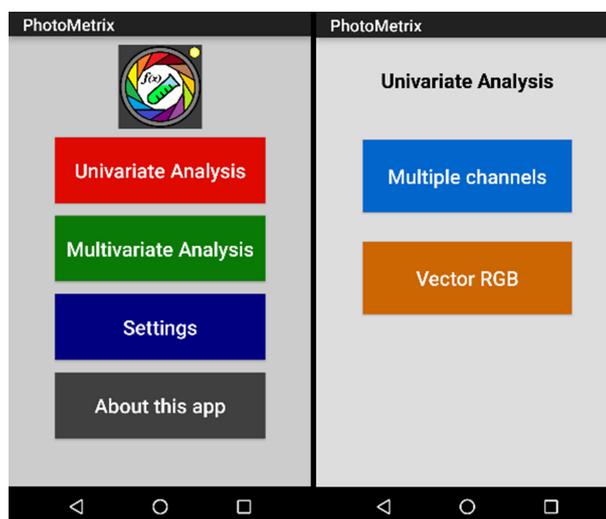**Figure 2.** PhotoMetrix® application interface, with univariate analysis options shown.

RESULTS AND DISCUSSION

Determination of fluoride in water

For the determination of aqueous fluoride using the conventional SPADNS method with spectrophotometric absorbance measurements, the calibration curve (y = -0.159x + 0.672) presented a coefficient of determination (R^2) of 0.990. In comparison, the smartphone-based colorimetric analysis using the PhotoMetrix® app generated a calibration curve (y = 35.813x - 1.585) with R^2=0.998 (Figure 3).

Since the PhotoMetrix® app uses the RGB norm vector standard as the analytical answer, the

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calibration model always has a positive slope, unlike the spectrophotometer, which uses absorbance values [32,35].
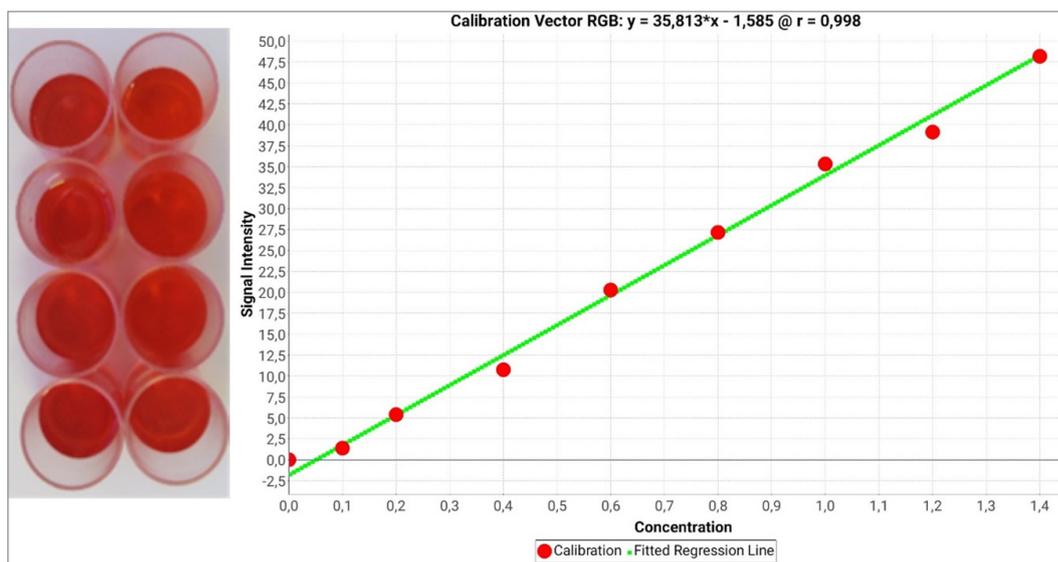
Figure 3. Standard solutions used to create the calibration curve (left) and the calibration plot (right) for fluoride determination with the PhotoMetrix® application [amount of shade × fluorine concentration (mg L^{-1})].

For the spectrophotometric analysis of fluoride, the LOD and LOQ were estimated to be 0.08 and 0.10 mg L^{-1}, respectively. In the PhotoMetrix® app, the corresponding LOD and LOQ values were estimated to be 0.05 and 0.10 mg L^{-1}. These values show the equivalence of fluoride determination acquired through a smartphone-based colorimetric analysis using the PhotoMetrix® app relative to the conventional method.

After establishing the calibration curves and the LOD and LOQ values, the natural and treated water samples were analyzed. Table I provides the fluoride results obtained by the conventional and PhotoMetrix® methods. No significant differences (p=0.6349, paired *t*-test) were identified between the two results.

Table I. Results obtained for the determination of fluoride (mg L^{-1}) (n=3)

Sample	Spectrophotometer	PhotoMetrix®
Raw water	1.06 ± 0.004	1.06 ± 0.005
Treated water 1	0.13 ± 0.004	0.13 ± 0.008
Treated water 2	0.42 ± 0.003	0.42 ± 0.005

As indicated in Table I, the raw water sample, which originated from an underground subterranean station, had a higher concentration of fluoride ions than the other samples. Nonetheless, the analyzed natural fountain water was still within the recommended standards for drinking water (1.5 mg L^{-1}). In comparison, the remaining samples presented lower fluoride concentrations because they had undergone treatment in the university itself, which aims to control the amount of fluoride in drinking water.

The samples analyzed by the SPADNS method and the colorimetric determinations made by different devices showed highly concordant values. For the raw water, the accuracy of the fluoride reading by the

PhotoMetrix® app relative to the spectrophotometric approach was 100.09%, and for the treated waters the accuracy was 98% and 100% for samples 1 and 2, respectively.

In previous work [25], fluoride determinations were performed using three different smartphones with the colorimetric analysis app, and the results were compared to the traditional ion-selective electrode technique. The accuracy values (87.6–105%) demonstrated good agreement among the procedure [25].

There are very few studies in the literature that describe the determination of analytes using mobile apps. However, due to several advantages, considerable growth in this research field is anticipated. Furthermore, our study, together with the results documented in similar work, leads us to believe that fluoride determination can be easily combined with the conventional spectrophotometric method (SPADNS) in an easy, fast, and reliable way using mobile devices.

Determination of phosphorus in water

Through the spectrophotometric determination of phosphorus in natural and treated waters, a calibration curve (y = 0.646x + 0.002) with an R^2 equal to 0.999 was obtained. With the PhotoMetrix® app, the calibration curve obtained (y = 414.602x + 1.638) had an R^2 value of 0.999 (Figure 4).

The LOD and LOQ were 0.012 and 0.018 mg L^{-1}, respectively, for the spectrophotometric determination of phosphorus and 0.010 and 0.019 mg L^{-1}, respectively, for the PhotoMetrix® approach. The LOD and LOQ for the analysis of phosphorus in both methods were similar and very low, being appropriate even for the determination of low concentrations of phosphorus.
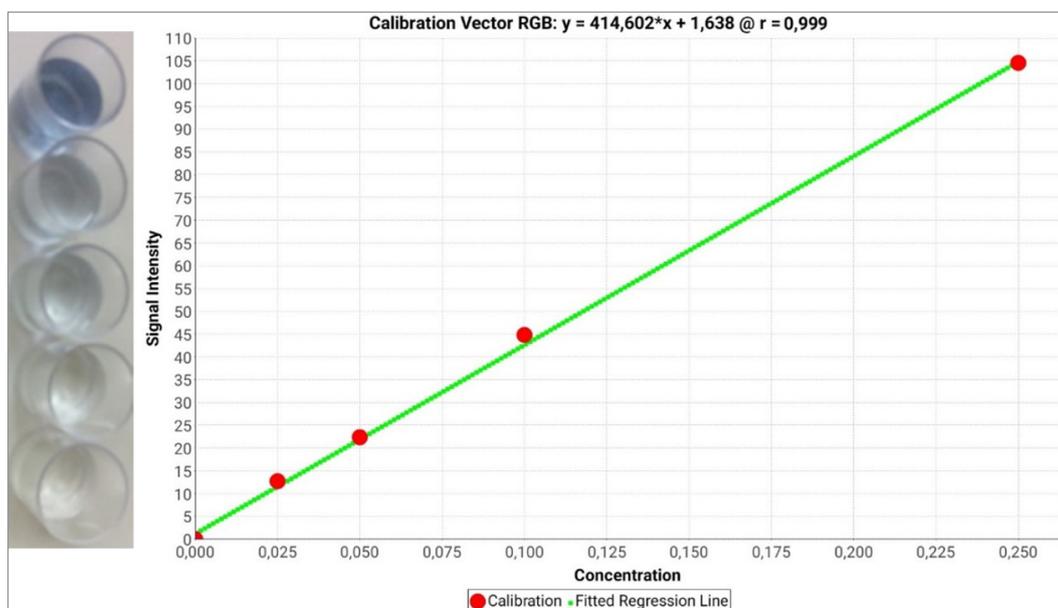
Figure 4. Standard solutions used to create the calibration curve (left) and the calibration plot (right) for phosphorus determination using the PhotoMetrix® application [amount of hue × phosphorus concentration (mg L^{-1})].

The results obtained for the detection of phosphorus in water samples using the respective reference and PhotoMetrix® methods are presented in Table II. No significant differences (p=0.4226, paired *t*-test) were identified between the two results.

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Table II. Results obtained for the determination of phosphorus (mg L^{-1}) (n=3)

Sample	Spectrophotometer	PhotoMetrix®
Raw water	0.249 ± 0.0009	0.250 ± 0.0010
Treated water 1	0.044 ± 0.0005	0.044 ± 0.0030
Treated water 2	0.051 ± 0.0008	0.051 ± 0.0023

The concentrations of phosphorus found in the treated water samples were within the limits established by Brazilian legislation (maximum phosphorus concentration of 0.15 mg L^{-1} in non-polluted waters). Moreover, it is possible to verify the agreement between the new method of colorimetric analysis and the spectrophotometric approach, considering an accuracy of 100.4% for the natural water and 100% for the treated waters.

A comparative analysis was conducted between the fluorine and phosphorus concentrations obtained by the reference method and those presented by the app for the three water samples. No significant differences between the two methods of quantification were identified ($p > 0.05$, paired *t*-test).

The proposed method uses the same analytical procedure as the reference method; therefore, the use of PhotoMetrix® does not result in a reduction in reagents and materials. However, there is a substantial gain in the time of analysis, the mobility, and the obtaining of results. These benefits arise because the app generates the analytical curve and superimposes the values of the samples directly on the calibration curve, while simultaneously providing the results of the analysis.

CONCLUSIONS

The study allowed for the development of a new analytical method for the analysis of fluorine and phosphorus using a mobile device app. The assay was applied to natural and treated waters; however, it can be expanded to a wide variety of samples. The analyses carried out by the conventional method and with the PhotoMetrix® app presented concordant values. Also, the new technique exhibited satisfactory figures of merit. The efficiency of this new analysis tool for the determination of fluoride and phosphorus ions present in treated and natural waters highlights its potential for rapid and accessible analysis. Moreover, it represents a valuable method for field analysis and for use on an industrial scale and in a school environment. The developed method also presented advantages when compared to the conventional method because it reduces the analysis time, it enables greater mobility, and it offers a significant increase in the analytical frequency. In addition, the PhotoMetrix® app allows for results to be sent by e-mail in real time to various registered consumers or authorities responsible for the water supply system.

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