Smartphone-based colorimetric determination of fluoride anions using polymethacrylate optode

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ABSTRACT

We developed a new transparent polymer optode based on polymethacrylate with Zr(IV) and alizarin red complex immobilized into it for digital colorimetric and solid-phase spectrophotometric determination of fluoride anions. The matrix changes its colour from purple to yellow after it contacts fluoride anion. We developed a processing algorithm for coloured images which helps calculate mean value for the RGB colour-coordinate system in a selected optode image and translates it into a fluoride concentration value. The analytical signal of the suggested method has a linearity range of 0.1–30 mg·L^{-1} with the detection limit 0.03 mg·L^{-1}. Compared to other methods, the modified polymethacrylate matrix is actually a ready-to-use colorimetric system offering rapid results for drinking water quality control.

1. Introduction

Lately, the interest towards determination of fluoride anion has risen significantly. The need for determination of this anion is concerned with contamination of the environment with toxins, pesticides and also the needs of the drinking water control system [1]. As the industry producing fluoride-containing products develops, contamination of the environment with fluoride becomes increasingly aggravating. Both excess and lack of fluorides in the human body affects thyroid, liver and other organs [2]. At the same time, presence of fluoride in water indicates its microbiological safety, besides, fluorides are also added to toothpastes and drinking water [3,4]. There is the recommended fluoride content range of 0.3–0.5 mg·L^{-1}, which rules out any possible toxic effects upon the human body from excess fluoride contained in water [5].

There are a large number of analytical methods for determination of fluoride in water available, such as electrochemical methods [6–8], chemiluminescent [9], chromatography [10,11] and fluorescent [12] ones. The most widely used methods are direct potentiometry using fluoride-selective electrode and photometry [13,14]. For routine determination of fluoride anion in water in the concentration range of 2.0–200.0 mg·L^{-1} potentiometric analysis is used due to its rapidity and

lower cost. The photometric method is used for analysis of the water samples with low content of fluoride ions <2.0 mg·L^{-1}. Thanks to their higher sensitivity and repeatability, sorption spectroscopic and visual photometric methods using chromogenic complex-building reagents are the standard ones used for determination of fluorides in tap water, water reservoirs and the industrial waste-water. Such analysis is based on the substitution reaction, in which fluoride anion displaces the organic ligand from the metal complex formed by such metals as Fe (III), Al (III), Th (IV), Zr (IV) etc., which is accompanied with a colour change. The chromophoric reagents [15] used are: Arsenazo I, alizarin red, morine, 8-oxyquinoline, eriochrome red, thorin, chrome violet. For example, photometric determination of fluoride anion concentration in water is based on formation of a complex organic compound of alizarin red, Ce (III) and fluoride anion by the ratio of 1:1:1 [16]. For example, smartphone-based colorimetric device demonstrated for determination of fluoride on the site of sample acquisition [17] involving discoloration of the paper with Zr(IV) and alizarin red complex immobilized into it after its contact with a fluoride solution in the concentration range of 0.2–200 mg·L^{-1}. Depending on the nature and transparency of the carrier substance, either absorption or diffused reflection of the light flux as well as the colorimetric characteristics of the chemical optical sensors are used for registration of the analytical response. The change

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in the colour of the complex in the presence of fluoride is rich in contrast, yet uneven change in the colour on the surface of a non-transparent carrier impedes reproducibility of the analytical signal. We suggested a new solution [18], which implies that the reaction between the AR-Zr (IV) complex evenly spread within the matrix and the fluoride takes place in a transparent polymer.

The advantages of the colorimetric method are sensitivity, simplicity, rapid reaction, simple analysis tools and easily detectible response of colour change in the presence of various substances [19]. By determination of fluorides a sensor's selectivity and sensitivity stem from the fact that fluoride is the smallest anion with the greatest electronegativity, which is capable of building very strong hydrogen bonds and act as a displacing ion by disruption of the coloured complexes.

The latest trend in the development of the colorimetric methods is concerned with digital image processing [20], which is actively used in chemical and biological analysis for a wide range of coloured substances. The typical examples include optical mobile platforms for colorimetry and the use of the digital image processing software. When a smartphone is used, the image of a coloured optode, paper or solution is made using an in-built camera and then it undergoes mathematical processing [21,22]. This processing is concerned with digitalization of brightness and tone, determination of transparency or light reflection intensity or spreading out of the general colour into the RGB channels.

The number of solid transparent polymer materials for spectrophotometry is small as combining the capability for solid-phase extraction and the capability of the chromogenic reagents to engage into an analytical reaction in a transparent solid phase without losing the matrix transparency is a significant problem. By the development of the optical media functioning by means of light absorption measuring, either individual transparent polymers such as Nafion [23] and polyvinyl chloride [24] or binary combinations of hydrophobic and hydrophilic polymers [25] are used as matrices for immobilization of the reagents. Combining a hydrophobic scaffold with a hydrophilic filling to build a transparent hybrid matrix is a currently relevant and actively developing approach; such "double" matrices with hydrophobic scaffold and introduced hydrophilic chains are represented as the following options: substituted derivatives of acrylic acid with polyethylene glycol (PEG) [26]; a combination of methacrylic acid, PEG and divinylbenzene [27], methacrylate-acrylamide-PEG solid-phase extractant plates [28]. Such polymer matrices are promising as ready-to-use analytical sensors for solid-phase spectrophotometric determination.

Carrying out colorimetric determination within the sensor instead of its surface makes it possible to avoid the errors concerned with the following: 1) uneven spatial distribution of the complex in the sensor; 2) incomplete reaction; 3) precipitation or formation of colloid [29–32]. The other advantage is the sensor's stable transparency, which makes it possible to use a sheet of white paper as a background [33]. Thus, all changes equally influence both the background and the sensor, which makes it possible to subtract the background from the digital image. This allows us to sufficiently lower the errors due to different lighting levels and the distance between a camera and a sensor. There are some similar works available featuring transparent gels [34,35], but our polymer matrix is a solid phase, which can be stored and used multiple times for colorimetric or spectrophotometric determination over a long period of time after the analysis has taken place.

We offer a transparent matrix based on polymethacrylate scaffold integrated with hydrophilic modifier, PEG 400, and modified by the reagents immobilized into it. It provides for direct detection of anion both by solid-phase spectrophotometry and visually [36]. The goal of this work was to study the possibility of smartphone-based determination of fluoride anion by the change in the colour of polymethacrylate matrix (PMM) with Zr(IV) and alizarin red (AR) complex immobilized in it.
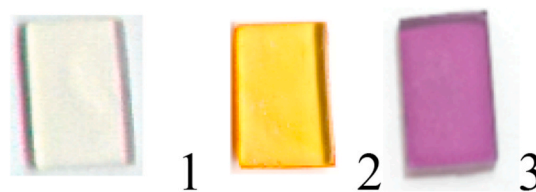

Fig. 1. Image of the initial PMM (1), the PMM with AR immobilized into it (2) and the PMM with AR–Zr(IV) complex.

2. Experimental

2.1. Immobilization of the chromogenic agent into the polymethacrylate matrix

PMM is used as a transparent analytical medium thanks to the hydrophilic elements of the PEG chain and the hydrophobic polymer scaffold of polymethylmethacrylate it contains. The optical analytical medium is provided in the form of plates obtained by block polymerization of methacrylic monomers in the presence of hydrophilic PEG and calcium methacrylate, which serves as a bond chain. Polymerization was carried out at the temperature of 60 $^{\circ}$C during 3 h in the presence of benzoyl peroxide. The obtained PMM samples were transparent colourless plates sized $4 \times 6 \times 0.5$ mm.

While choosing the reagent to be immobilized into the matrix we followed the requirements towards the colour reaction for fluoride determination, which is supposed to be sensitive, contrastive, selective and rapid at room temperature. The reagent and the complex obtained are supposed to be slightly-soluble in water solutions and securely retained within the polymer phase. In order to determine fluoride anion we used their ability to form stable complexes with Zr(IV), which results in destruction of the colour of the complex AR–Zr(IV).

The process of the PMM modification was carried out in two stages. During the first stage the initial sample was held in the 0.01 M water solution of AR in the presence of an acetate buffer. After that, the plate with AR immobilized into it was held in the 0.01 M water solution of ZrOCl$_2$. As a result, we obtained the transparent plates coloured red-to-purple (Fig. 1), which we used as optical sensors.

2.2. Determination of fluorides

For determination of fluoride anion 1 ml of 2M HCl was added to 50 ml of water, after which a PMM plate with AR–Zr(IV) complex immobilized in it was immersed into the solution for 20 min. After that the PMM plate was taken out, dried using filter paper and its optical density (*A*) was measured. We did use a blank sample in our work; its absorption was taken as the zero value. The lighting has the same influence on the sensor and on the white paper background used with our transparent polymer matrix. The difference between optical density values of the blank PMM and after its contact with the solution analysed at the absorption band maximum of 520 nm for AR–Zr(IV) complex, was taken as the analytical response. For the colorimetric determination the optode was placed on a white sheet of paper and photographed using a smartphone. We used the software we developed to process the digital image; it fixed the colour intensity of each area of the digital image and represented each pixel as a non-linear combination of RGB channels.

2.3. Reagents

The precursor solution containing sodium fluoride (NaF) with the concentration of 1 g·L^{-1}, the 0.01 M solution of Zr (IV) from ZrOCl$_2$·8H$_2$O and the 0.01 M AR (Sigma-Aldrich, CAS 130-22-3) was prepared by dissolving precisely weighted amounts of the substances in double-distilled water. The working solutions with different NaF concentrations were obtained by adding double-distilled water to the
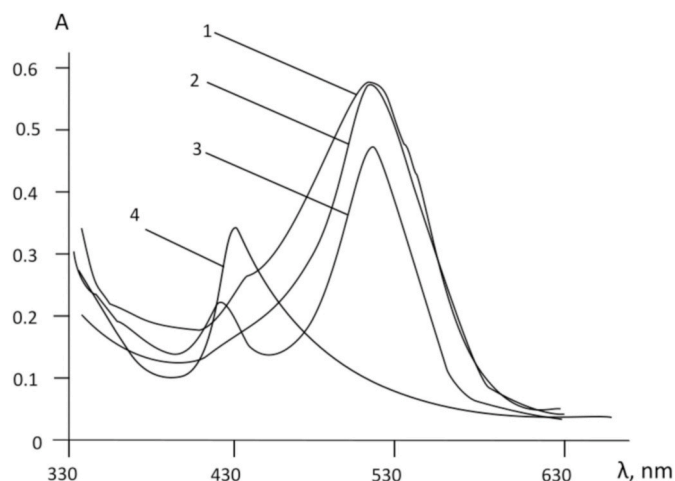
Fig. 2. The absorption spectra of AR–Zr(IV)in water solution (1), in PMM (2) and after the contact with the fluoride anion solution with concentration level of 5 mg·L^{-1} (3) and 20 mg·L^{-1} (4).
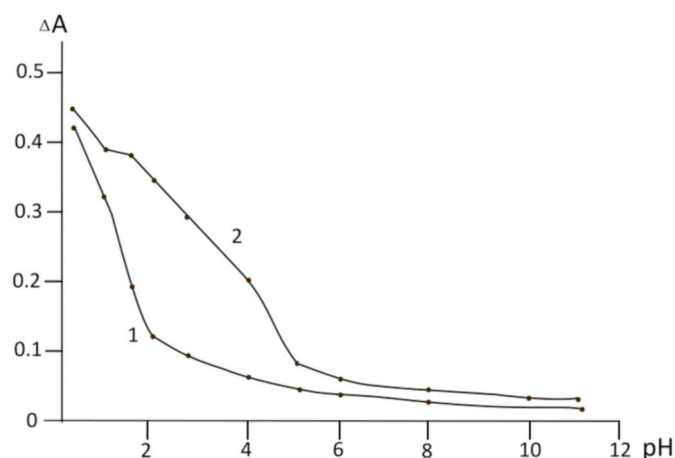

Fig. 3. The changes in the optical density of PMM-AR–Zr(IV) depending on the solution pH in the absence (1) and in the presence (2) of 5 mg·L^{-1} of fluorides.

precursor solution on the day of experiment. Before the solutions were used, 1 ml of concentrated HCl was added to them in order to change their acidity to pH 2 as associates of fluoride anion break up in a medium with such acidity level. All reagents (Dynamic Products Ltd, India) were used without any additional purification.

2.4. Apparatus

In our work we used MultiBioRS-24 multirotator (Biosan, Latvia), SHIMADZU UV -1800 spectrophotometer (Shimadzu, Japan). Colour intensity of each digital image area was fixed using a Samsung A70 smartphone with a 12 mpx camera. The laboratory conditions were the following: light from the daylight fluorescent lamps, the distance between the camera and the sample was 10–15 cm, the pictures were taken without using ultra-close-up photography in the Auto mode. We averaged out the colour value on the selected area of the sensor's digital image, which usually comprised 90–95% of its surface.

3. Results and discussion

3.1. Spectrophotometric determination of fluoride
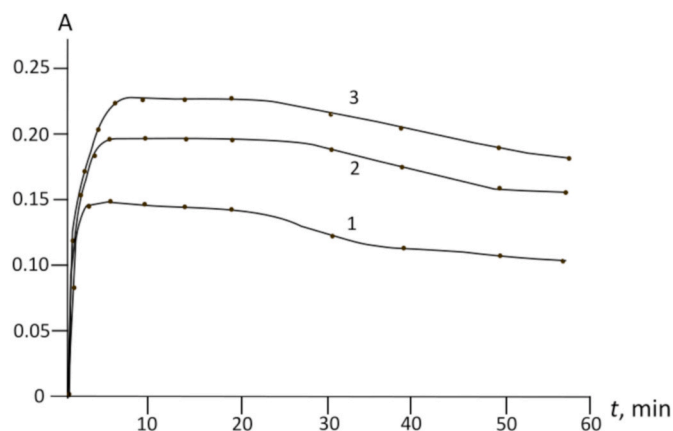
Transparent PMM plates modified with AR–Zr(IV) were used for

Fig. 4. The relation between the analytical signal of PMM-AR–Zr(IV) and the time of its contact with the fluoride solutions, C, mg·L^{-1}: 1 – 1; 2 – 5; 3 – 10.

Fig. 5. Discolouration of PMM-AR–Zr(IV) in the presence of the ions, the concentration for each of the ions being 40 mg·L^{-1}: 1 – Cl^{-}, Br^{-}, I^{-}; 2 – SO$_4^{2-}$, PO$_4^{3-}$; 3 – the mixture of 1 + 2; 4 – F^{-} + mixture 3; 5 – mixture 3 by pH level of 1; 6 – mixture 3 with doubled concentration.

determination of fluoride anion in solutions. The absorption spectrum of the modified PMM plates is presented in Fig. 2. The absorption maximum of AR–Zr(IV) in the polymer phase is 520 nm, and its absorption maximum in a water solution is the same. The relation between the optical density and fluoride concentration is linear within the interval of 0.3–20 mg·L^{-1}.

Determination of fluorides is carried out in an acidic environment in order to break up associates and fluoride complexes of metal ions [37]. However the immobilized AR–Zr(IV) itself breaks up in an acidic environment, both in a polymer matrix and in solutions. Fig. 3 presents relations between the optical density of the modified PMM and the pH level in the range of 2–11. When pH < 2, the AR–Zr(IV) complex breaks up and PMM entirely discolours to yellow irrespective of the presence of fluorides. In the range of 2<pH<4 we see a significant difference in the optical density value in the absence and in the presence of fluoride anion. By pH>5 the reaction of AR–Zr(IV) complex destruction by the fluoride anion present in the solution does not take place. Hence, the pH range of 2–3 is the optimal one for the analysis to be carried out in.

As PMM-AR–Zr(IV) contacts fluoride solution we see rapid analytical reaction in the polymer phase. Fig. 4 shows how analytical signal changes depending on the contact time. These relations are classical ones and the colour signal stabilizes in 10 min.

The decrease in the optical density we see starting 25–30 min is due to polyethylene glycol being washed out of the PMM. The optical density is stable and remains unchanged during a few weeks if the extraction time is up to 20 min, after which PMM is removed from the solution.

3.2. Influence of the interfering ions

In order to study the influence of the interfering ions we carried out determination of a fluoride in the presence of both Cl^{-},Br^{-},I^{-}, HSO$_4^{-}$, H$_2$PO$_4^{-}$ anions and metal cations. Fig. 5 shows that only the fluoride anion caused a significant change in the colour of the sensor, while adding any other anions caused no obvious changes. H$_3$PO$_4^{-}$ and AcO^{-} caused an insignificant decrease in the discolouration intensity, which

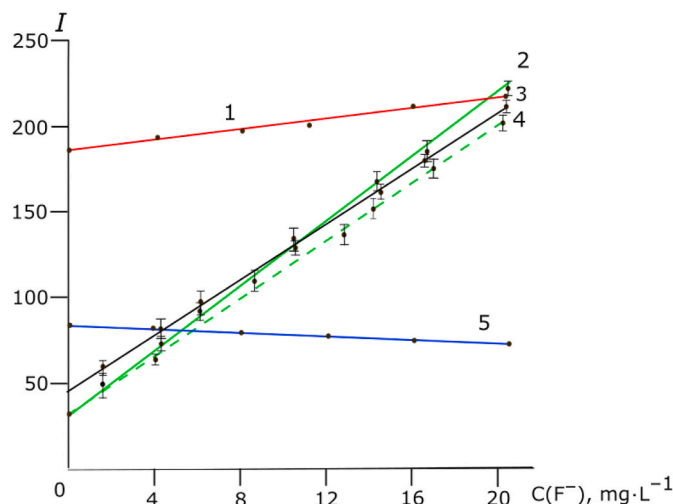**Fig. 6.** Colorimetric scale of the PMM-AR–Zr(IV) plates for determination of fluorides.

Fig. 7. Relations between the intensity of the R, G, B channels and the concentration of the fluoride anion in the solution for image of the PMM-AR–Zr(IV) colour scale: 1 – red ch.; 2 – green ch.; 3 – gray ch.; 4 – green ch. in solution of mixture 4 (Fig. 5); 5 – blue ch. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

was due to breakup of the complex in the highly acidic environment. The experiment results revealed that PMM-AR–Zr(IV) can become a selective sensor with real-time colorimetric response.

3.3. Colorimetric determination of fluoride

In the presence of fluoride anion the colour of the matrix changes to yellow as a result of the breakup of AR-Zr(IV). The concentration of the fluoride anion was visually determined by comparing the colour of PMM-AR–Zr(IV) to the colorimetric scale (Fig. 6) obtained by scanning real-life samples.

We developed a set of mathematical tools for colorimetric analysis using a transparent PMM as a sensor. The digital signal obtained through the colour change in a variety of reference systems is a colorimetric

characteristic associated with the concentration of the analyte in the sample. For the colorimetric determination of fluorides the smartphone was used as the colorimetric device for obtaining and processing of the optode images. The software split optical density of each pixel of the digital image into individual intensity levels I of the R, G, B colour channels (Fig. 7). Also, we calculated the dependence of the concentration on the gray value index according to the work's algorithm [38]. The algorithm of the gray value index calculation based on the RGB channel intensity is promising and helps reduce random inaccuracy due to variable lighting conditions for a non-transparent sensor. In our case the dependencies for the gray and for the green channels are close as the lighting influences both the sensor and the white paper background we use for our transparent polymer matrix the same way.

The calibration curves using the observable optical density spread into the R, G, B channels differ both in terms of tilt and linearity range. Since by the contact of PMM-AR–Zr(IV) with the fluoride solution we, as expected, see discolouration to yellow, the brightest channel is green (G). The linear intensity range of $G = (43.8 \pm 0.7) + (722 \pm 11) \cdot C_{F^-}$ channel completely comprises the spectrophotometric range and amounts to 0.1–30 mg·L^{-1} with the correlation coefficient (r) 0.9993. In the framework of the conditions of the experiment involving the use of a smartphone the detection threshold value 0.03 mg·L^{-1} was calculation by 3S criterion [39], which is below the detection level of 0.1 mg·L^{-1} measured by a spectrophotometer.

The comparison of the methods points at the fact that with the help of the digital image obtained using the smartphone and the appropriate image processing software it is possible to carry out determination of fluoride anion concentration with the same sensitivity that solid-phase spectrophotometry offers. At that, the colorimetric method is more reliable as it is not based on the use of a single response at a certain wavelength as it is done by solid-phase spectrophotometry, but on the efficient use of all of the spectral information, instead.

The colorimetric determination method using digital image processing software was tested by tap water analysis. Table 1 provides the metrological characteristics of fluoride anions concentration determination using the PMM-AR–Zr(IV) solid-phase spectrophotometry. Accuracy of the suggested method was evaluated by the results of determination of bromate added in samples of bottled drinking water. In order to evaluate the accuracy, accuracy index (σ), which is the ratio of the difference between the concentration determined (mean value) and the concentration value entered to the value entered, expressed as a percentage, was used. Precision of the analysis results under the repeatability conditions was measured by the relative standard deviation rate (s_r).

Table 1
Comparison of the results of solution spectrophotometric (SPM), solid phase spectrophotometric (SPS) and smartphone based colorimetric (SBC) determination of the fluoride anions in waters using PMM-AR–Zr(IV).

Samples	$C_{F^- \text{ spiked}}$, mg·L^{-1}	SPS			SBC			SPM		
		$C_{F^- \text{ found}}$, mg·L^{-1}	s_r, %	σ,%	$C_{F^- \text{ found}}$, mg·L^{-1}	s_r, %	σ,%	$C_{F^- \text{ found}}$, mg·L^{-1}	s_r, %	σ,%
Tap water 1	0.5	0.52 ± 0.04	3.1	−4.0	0.52 ± 0.02	1.5	−4.0	0.5 ± 0.1	8.1	0.0
	2.0	2.1 ± 0.2	3.8	−5.0	2.0 ± 0.1	2.0	0.0	2.0 ± 0.4	8.0	0.0
Tap water 2	1.0	0.98 ± 0.09	3.7	2.0	1.03 ± 0.08	3.1	−3.0	1.1 ± 0.2	7.3	−10.0
	5.0	5.1 ± 0.4	3.2	−2.0	4.9 ± 0.2	1.6	2.0	4.9 ± 0.2	1.6	2.0
Ground water 1	0	0.12 ± 0.03	10.1	–	0.16 ± 0.03	7.6	–	0.2 ± 0.1	20.1	–
	0.5	0.48 ± 0.09	7.0	4.0	0.52 ± 0.09	7.0	−4.0	0.5 ± 0.1	8.1	0.0
	1.0	1.1 ± 0.2	7.3	−10.0	1.1 ± 0.2	7.3	−10.0	1.2 ± 0.3	10.1	−20.0
Ground water 2	0.5	0.55 ± 0.07	5.1	−10.0	0.53 ± 0.05	3.8	−6.0	0.5 ± 0.1	8.1	0.0
	1.0	1.1 ± 0.2	7.3	−10.0	0.97 ± 0.09	3.7	3.0	1.0 ± 0.1	4.0	0.0
Ground water 3	1.0	1.0 ± 0.2	8.1	0.0	1.1 ± 0.1	3.7	−10.0	1.0 ± 0.2	8.0	0.0
	2.0	2.1 ± 0.3	5.8	−5.0	2.1 ± 0.2	3.8	−5.0	2.0 ± 0.3	6.8	0.0

As Table 1 shows, the fluoride concentrations measured using the colorimetric optode correspond very well with the specific spectrophotometer. The results obtained are satisfactory (s_r does not exceed 10%) and attest to accuracy and repeatability of the suggested method of fluoride anions determination.

4. Conclusion

We developed a smartphone-based colorimetric analysis method involving digital processing of an image of a coloured transparent PMM with the linear range of 0.1–30 mg·L^{-1} and the detection limit 0.03 mg·L^{-1}. Our work reveals that the maximal changes in the colour of the PMM modified with AR-Zr(IV) were attained by pH 2–4, the contact time being 10 min. The optical sensors and the methods we suggest can be used for visual monitoring of fluoride without using any standard spectrophometric equipment also. Stabilization of the complex AR–Zr (IV) and accumulation of fluoride in the polymer matrix makes the new portable colorimetric device appropriate for determination of fluoride anions in water samples containing low concentrations of the analyte, such as the tap water obtained from the end of a pipeline network.

CRediT author statement

Nadezhda Saranchina: Conceptualization, Methodology, Writing – original draft, Yurii Slizhov: Conceptualization, Validation, Yulia Vodova: Investigation, Validation, Nazgul Murzakasymova:: Investigation, Anzhelika Ilyina: Investigation, Nataliya Gavrilenko: Conceptualization, Validation. Mikhail Gavrilenko: Validation, Writing – original draft, Writing – review & editing.

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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