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Research Article

Native Fluorescent Natural Deep Eutectic Solvents for Green Sensing Applications: Curcuminoids in *Curcuma longa* Powder

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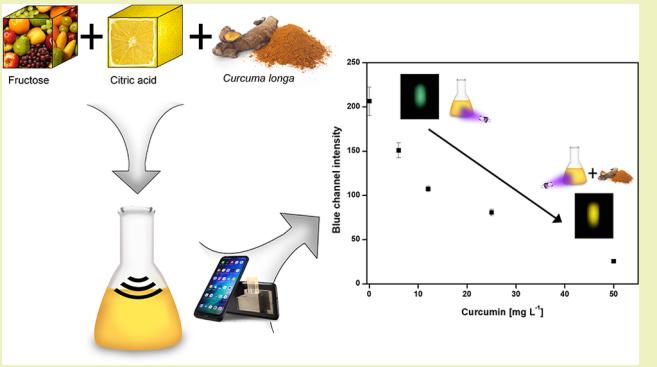
ABSTRACT: Natural deep eutectic solvents are a trending topic in Green Chemistry. These solvents present high solubilization capacity, reusability, tunable properties, simple preparation, biodegradability, safety, high availability, and low cost, making them excellent candidates for analytical applications. In this work, a new family of fluorescent eutectic systems is described, with the fluorescence property being unknown and unused so far. For this purpose, a novel preparation method using an ultrasound probe was employed, by means of an innovative single-step procedure, that included the preparation of FCH (fructose, citric acid, and water, 1:1:5 molar ratio) and the extraction/determination of curcuminoids from *Curcuma longa* powder. This methodology was successfully carried out by employing a portable and inexpensive 3D-printed fluorometer and a smartphone. In this way, extraction efficiencies between 90 and 106%, relative to the NIST reference method, were obtained in just 3.40 min. Besides, the greenness of the new methodology was evaluated by employing the AGREE metric, showing that the developed approach is >2.5 times greener than previously published works for curcuminoid determination. This groundbreaking procedure is robust, versatile, and simple to implement, does not require sophisticated apparatus or instruments in the detection step, and, mainly, agrees with Green Analytical Chemistry (GAC) principles.



KEYWORDS: *NADES, Fluorescence, Ultrasound probe, Curcuminoids, 3D-printed device, Green Analytical Chemistry, AGREE metric*

INTRODUCTION

Sustainability is a prime concern for chemists. Greening methodologies need a balance between analytical performance and Green Analytical Chemistry (GAC) principles.[1] Sustainable and efficient analytical methodologies involve the application of innovative tools, such as miniaturization, employment of truly green solvents, simplification of sample-preparation procedures, and use of portable and low-cost instruments.

Natural deep eutectic solvents (NADES) are the green solvents of the moment. High solubilization capacity, biodegradability, tunable properties, safety, reusability, simple preparation, high availability, and low-cost components make NADES excellent candidates for analytical applications.[2] These solvents are formed by mixtures of common cellular constituents such as sugars, amino acids, organic acids, and choline derivatives, whose main driving forces are hydrogen bonds, with melting points hundreds of degrees lower than those of the constituents.[3,4] NADES stand out for being design solvents with tunable physicochemical properties due to the large number of potential combinations of their components ($\sim 10^6$). They are also low-cost and require simple preparation procedures, enabling their synthesis at the time of use.[5,6]

To date, five methods have been reported for NADES preparation, which are heating and stirring,[6] evaporating,[6] freeze-drying,[7] microwaving,[8] and using an ultrasonic bath.[9] By far the most utilized preparation method is heating and stirring. However, this approach is time- and energy-consuming, with the greenness feature of the solvents obtained with this technique being controversial. Thus, the development of new and efficient methods for NADES preparation becomes crucial. In this sense, the use of ultrasound energy seems to be ideal. However, its synthesis using this system has been poorly explored.[9] Santana et al.[9] prepared some NADES using an ultrasonic bath for 45 min with acceptable results. In another approach proposed by Hsieh et al.,[10] the preparation was achieved also by means of a 5 h ultrasonic bath until a clear liquid was obtained. Although both methods demonstrated the feasibility of using ultrasonic waves for NADES preparation,

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Table 1. Abbreviation, Components, Molar Ratios, and Presence of Native Fluorescence of Tested NADES

abbreviation	component 1	component 2	component 3	component 4	molar ratio	native fluorescence
FCH	fructose	citric acid	water		1:1:5	yes
FGH	fructose	glucose	water		1:1:7.5	yes
FSH	fructose	sucrose	water		1:1:7.5	yes
FGSH	fructose	glucose	sucrose	water	1:1:1:11	yes
FLH	fructose	lactic acid	water		1:1:5	no
CClGH	choline chloride	glucose	water		5:2:5	yes
CClFH	choline chloride	fructose	water		5:2:5	yes
GLH	glycerol	lactic acid	water		1:1:1	no
LGH	lactic acid	glucose	water		5:1:9	no
CGH	citric acid	glucose	water		1:1:4	no

the application of an ultrasonic bath took too long, therefore making the process inefficient. Optimization of energy consumption in chemical processes is mandatory from the GAC point of view because energy generation and low consumption are essential for the environment.[8,11] In this sense, ultrasound probe systems have high cavitational intensity because acoustic energy is directly introduced in the liquid and the power is dissipated into the mixture. The probe system provides a stronger intensity, ∼100 times higher, than an ultrasonic bath,[12,13] thus making the system much more efficient.

NADES have been used by Kadyan and co-workers as media for studies of L-tryptophan fluorescence,[14] demonstrating that fluorescence quantum yields of the amino acid in the eutectic system are significantly higher in NADES than in water or organic solvents. To the best of our knowledge, there are no studies about the native fluorescence of NADES, with this property being unknown and unused so far. Intrinsic fluorescence of NADES represents a novel alternative with great potential for analytical applications, considering their tunability and ability to form organized media.[15]

Fluorescence-based detection has been extensively used for the design of sensors and biosensors.[16,17] 3D-printable analytical devices have lately attracted much attention from the scientific community due to their enormous advantages, such as low cost, unique portability, quick response, lightweight, flexibility, and, mainly, the possibility of in situ analysis.[18,19] Fluorescence may be a more suitable candidate for portable devices compared with UV detection because of its higher sensitivity and selectivity.[20]

Curcumin, the main curcuminoid of *Curcuma longa*, is a highly valuable product, being used since ancient times in the food and health industries.[21,22] Besides, the determination of curcuminoids is a challenging analytical task considering their water insolubility and high degradability.[23] The procedures available for the extraction of curcuminoids include Soxhlet and liquid extraction mediated by ultrasound and microwave, among others.[23−26] Some works have been previously reported for the extraction of curcuminoids from *Curcuma longa* employing NADES. Liu et al. developed a method using CGH (citric acid/glucose/water, 1:1:4) and heating and stirring.[23] Moreover, the use of an ultrasound (US) probe to extract turmeric using a NADES has been reported by Patil et al.[24] In that work, the eutectic solvent was synthesized prior to the extraction step, by means of the conventional heating and stirring method during 2 h. In a subsequent step, US energy was applied to extract curcuminoids (20 min). It is important to clarify that only organic solvents, and exclusively those recommended by the Expert Committee, can be used to carry out this procedure.[27] Considering that organic solvents are toxic and thus not edible, they must be removed before the addition of curcuminoid extracts in food and health products, usually via evaporation, chromatography, or crystallization, which are noncost-effective procedures and involve a high number of steps, with the consequent risk of analyte degradation.[28,29]

Interestingly, NADES have been proposed as the third solvent in living cells, together with aqueous and lipidic media.[30] Additionally, NADES could interact with analytes through hydrogen bonds, enabling the development of multiple analytical extraction schemes.[8] The latter explains their high solubilizing capacity of natural compounds.[31,32]

Thus, the main objective of this work is to present, explore, and apply the new fluorescence property of some NADES. In this way, an innovative method for the preparation of NADES using an ultrasound probe was employed. Taking advantage of this highly useful fluorescence property, the extraction and determination of curcuminoids in a single step is presented using a 3D-printed fluorometer and a smartphone camera. Finally, the Analytical Greenness metric approach was applied,[33] and scores were compared with recent reports for the extraction/determination of curcuminoids.

EXPERIMENTAL SECTION

Materials. Choline chloride (≥98%), sucrose (≥99.5%), and glucose (99.5%) were purchased from Sigma-Aldrich (St. Louis, MO, U.S.A., https://www.sigmaaldrich.com/). Citric acid (99.5%), ethanol (92.3−93.8% w/w), methanol (99.8%), lactic acid (88.0−90.0%), glycerol (99.5%), and fructose (99.0%) were acquired from Anedra (Buenos Aires, Argentina, https://www.research-ag.com/). Standard curcumin (C.I. 75300) was acquired from Biopack (Buenos Aires, Argentina, https://www.biopack.com.ar/). Ultrapure water (18.0 MΩ·cm) for NADES preparation was obtained from a Milli-Q system (Millipore, Bedford, MA, U.S.A., https://www.merckmillipore.com/). Five commercial turmeric rhizome powders (*Curcuma longa*) were purchased in local shops in Bahía Blanca, Argentina.

Instrumentation. An ultrasonic probe (Sonics Vibra Cell VCX 130, titanium probe tip of 9.5 mm diameter, 20 kHz frequency, 130 W nominal power) was employed for NADES preparation and curcumin extraction. For fluorescence detection, a smartphone-based 3D-printable device previously designed by our group[34] and slightly modified was employed. An ultraviolet (UV) light-emitting diode (LED) (390 nm, 0.1 W, 8 mm, Patagoniatec, Buenos Aires, Argentina) was used. ImageJ (https://imagej.nih.gov/) was used for image and data processing. An Agilent 8453 spectrophotometer (Agilent Technologies, CA, U.S.A.) was employed for a validation study.

Data Analysis. All statistical parameters were calculated using Microsoft Office Excel 2010 (Microsoft, Redmond, WA, U.S.A.). Green metrics were calculated by employing the AGREE (Analytical

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Greenness) metric approach and software (https://mostwiedzy.pl/AGREE).[33]

NADES Preparation. A new method to obtain NADES using an ultrasonic probe is presented. In this sense, the solid components were placed in a 50 mL centrifuge tube and the appropriate amount of water was added (see Table 1). Then, the ultrasound tip was placed in the center at 1 cm from the bottom of the tube, and US energy was applied by means of cycles (20 s on, 10 s off) at 91 W of power (70% of amplitude).

Standard Working Solutions. The calibration standards were built (n = 3) by adding the curcumin before the FCH preparation. Because of the fact that the calibration curve was exponential, a logarithmic function was applied to the original curve, obtaining a linear response.[35] Calibration curves were prepared using curcumin in the concentration range 0−50 mg L^{-1}. The results were expressed in grams of curcumin per 100 grams of sample. In the case of the validation study, the standard working solutions were built in methanol, and the data were recorded at 425 nm.

Image Capture and Processing. A Samsung J7 Pro smartphone attached to the 3D-printed device was used to capture images in JPEG format. The 3D device was slightly modified by removing the collimator and bringing the LED closer to the cuvette (distance between LED and cuvette = 3 mm) in order to improve the fluorescence intensity. For excitation, an ultraviolet LED (390 ± 5 nm) was used. Capture-condition parameters were fixed in manual camera mode as follows: ISO 100, manual white balance (cloudy), shutter speed 1/17 s, opening value F1.7, and focal length of 3.71 mm. All image files were organized and processed as stacks with the ImageJ software in order to obtain the intensity of each channel (red, green, and blue), the average intensity, and the luminance value (set as (0.299R + 0.587G + 0.114B)). These parameters were studied, and the intensity of the blue channel was selected as an analytical response.

Application. To demonstrate the applicability and versatility of fluorescent NADES, a new, simple, and green way to perform curcuminoid extraction and detection from turmeric powder is proposed. This innovative process involves the formation of the fluorescent solvent and the extraction of the analytes at the same time in one single step. The appropriate amount of NADES components (citric acid, fructose, and water) were placed in a 50 mL tube, and 0.0500 g of turmeric powder was added. Then, the ultrasound probe was employed under the aforementioned conditions (see NADES Preparation section), obtaining the solvent and the extract at the same time.

For the validation study, the extracts were prepared according to the NIST Analytical Approach for Determination of Curcuminoids.[36] Commercial turmeric rhizome powder (0.1000 g) was placed in a tube, and 10.00 mL of methanol was added. The extraction was carried out by end-over-end rotation for 15 min followed by ultrasonication in a bath for 15 min. Then, the extracts were centrifuged during 10 min at 3000 rpm.

RESULTS AND DISCUSSION

Fluorescent NADES. Preliminary results using a UV LED and then employing a spectrofluorometer for confirmation revealed that some eutectic systems can generate unique new high-intensity fluorophores (Figures S1a and b and S2). To the best of our knowledge, this is the first time that the native fluorescence property of NADES is reported and applied for analytical purposes. The fluorescence of these solvents, together with all the previously described skills, makes NADES ideal candidates to be used in image sensing.

Selection of NADES. It is well-known that sound waves in a liquid media cause cavitation, consisting of the formation and collapse of bubbles. When the bubbles reach a critical size and implode, there is an abrupt release of high heat and pressure.[37] The energy released assists in the interaction between the hydrogen-bond donor (HBD) and the hydrogen-bond acceptor (HBA), leading to the formation of NADES.[9] Taking into account that the ultrasonic probe delivers the energy directly into the sample, it is logical to predict that, by using this method, NADES could be easily obtained. Keeping the aforementioned in mind, different combinations of fructose, citric acid, glucose, sucrose, lactic acid, glycerol, and choline chloride were tested (Table 1). All combinations studied in this work had to contain water in their structure because most of the components were solids and an ultrasound probe requires a liquid medium to propagate the ultrasonic waves. Figure 1 shows the analytical response of native fluorescent

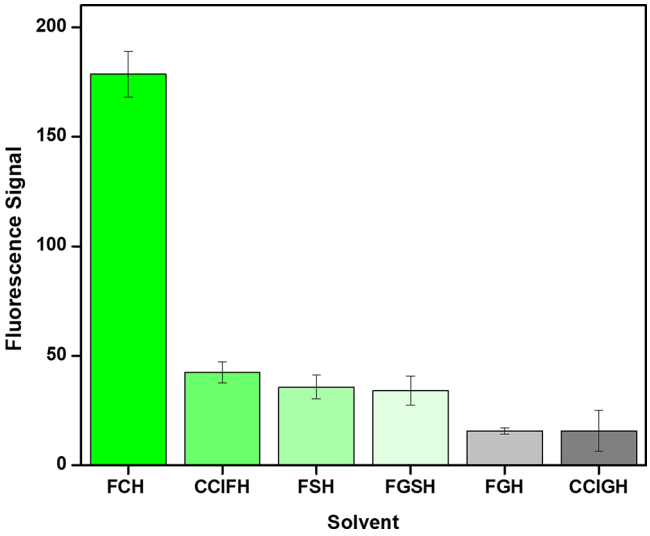

Figure 1. Fluorescence signals of evaluated NADES. The signal was obtained as the mean of the channels ((R + G + B)/3) (see Image Capture and Processing section for details of excitation and capture conditions). All experiments were performed in triplicate.

NADES acquired by means of a 3D-printed device coupled to a smartphone (see Instrumentation section). As can be seen, the solvent composed of fructose, citric acid, and water (FCH) shows the highest fluorescence signal, more than twice those of the other evaluated NADES. Then, to confirm that the fluorescence was attributable to the eutectic superstructure, the signal of the individual components was evaluated under the same molar ratios and preparation conditions (see NADES Preparation section). As can be seen in Figure 2, individual components show a negligible signal compared with FCH. Nevertheless, additional experiments are necessary to understand the mechanism of this behavior.

Our results could indicate that hydrogen bonds and rotatable bond counts (Table S1) are the main driving forces for the formation of fluorophores (Table 1 and Figure 1). Fluorophores formed as a result of the interaction between a five-carbon monosaccharide and a hydroxylated tricarboxylic acid showed the highest fluorescence intensity (Figure 1). The latter could be explained considering the number of hydrogen donor/acceptors (a total of 22 in FCH) and the much higher rotatable bond count of citric acid compared to lactic acid (5 vs 1).

Optimization of FCH Preparation. Taking into account the obtained results, FCH was selected for further experiments. Fluorescence intensity was monitored in order to evaluate how the ultrasound probe parameters affected the preparation of FCH. The following variables were sequentially evaluated in a

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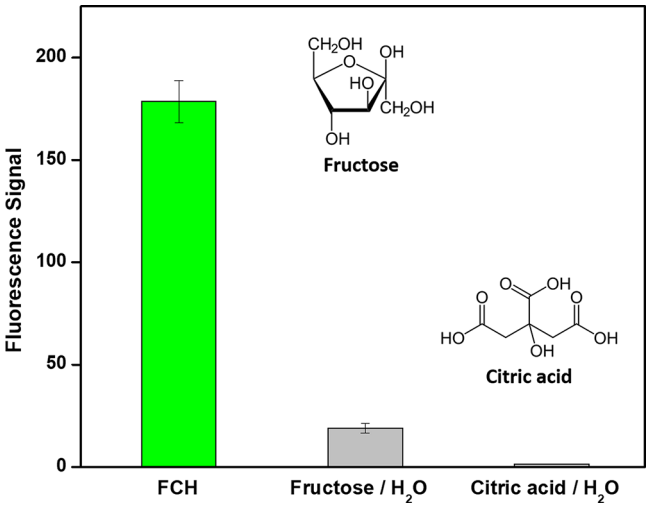

Figure 2. Fluorescence study of FCH individual components. The signal was obtained as the mean of the channels ((R + G + B)/3). (Inset) Chemical structures of involved compounds (see Image Capture and Processing section for details of excitation and capture conditions). All experiments were performed in triplicate.

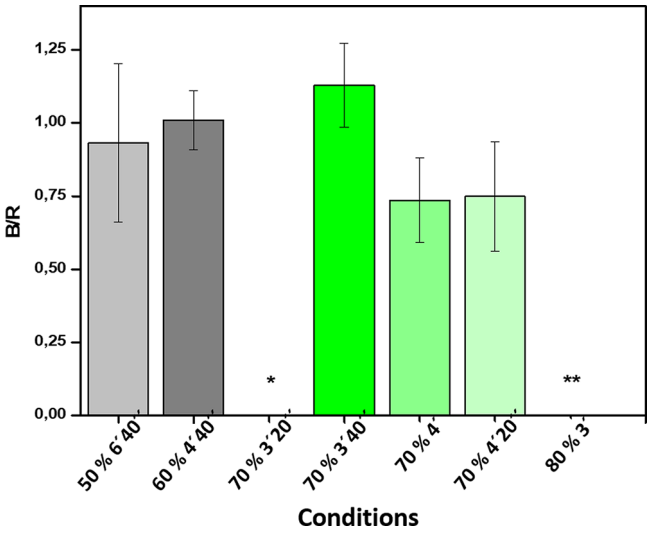

Figure 3. Optimization of ultrasound probe variables for FCH preparation. (*) Indicates particles in suspension; (**) indicates temperature resulted in aborted procedure (see Image Capture and Processing section for details of excitation and capture conditions). All experiments were performed in triplicate.

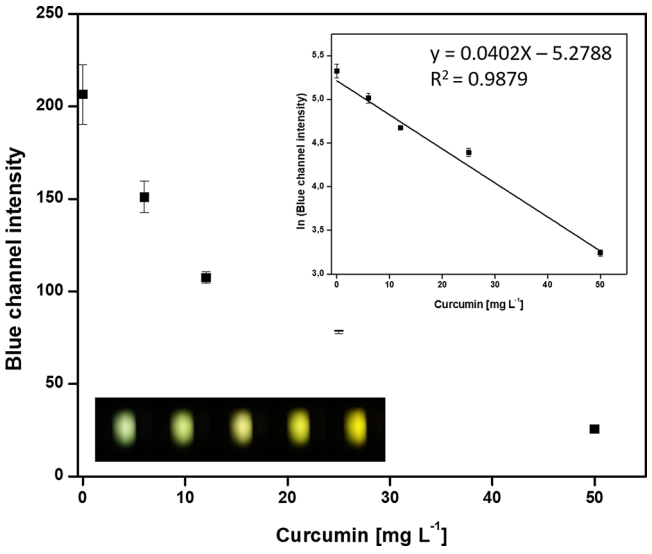

Figure 4. Exponential and linear (inset) calibration curves of curcumin. Real photographs of each working solution (inset). (See Image Capture and Processing section for details of excitation and capture conditions.) All experiments were performed in triplicate.

univariable way: cycles, power, and time. An ultrasonic cycle is defined as the sonication time (on) and the intermittent time (off). It was observed that, when working under short ultrasonic cycles (<20 s on−10 s off), the temperature of the system was too high because it exceeded the temperature allowed by the ultrasound manufacturer (100 °C). The latter was attributed to insufficient intermittency time. This situation involved an interruption in the sonication process without the complete interaction of the solid components in NADES. On the other hand, when working at long cycles (>20 s on−10 s off), the same behavior was reached due to an excess of US application time (excess of "on" time). For all these reasons, 20 s on and 10 s off were selected as the optimal values.

The power was tested between 50 and 80% (nominal power 130 W). Values lower than 50% were discarded with the aim to obtain shorter preparation times, and >70% caused an abrupt increase in temperature, again aborting the sonication process. All ultrasonic power studies were evaluated until a clear liquid was obtained. Once this variable was selected (Figure 3), the effect of increasing time was evaluated. The selected power was 70%; after that, times longer than 3 min 40 s were tested. It is important to mention that values lower than the aforementioned were insufficient to get the eutectic system; instead, translucent solutions with solids in suspension were observed. So, as can be seen in Figure 3, the best analytical signal was obtained at 3 min 40 s. The total fluorescence intensity was stable for at least 20 days.

It should be noted that the blue channel was selected as the analytical response, taking into account that it showed the highest sensitivity for the analytes under study at the application step. At times higher than 3 min 40 s, FCH decreased the signal intensity, acquiring a darker color and thus affecting the emitted blue−red channel ratio (the red channel intensity exceeded that of the blue channel), which could affect the sensitivity of the system.

Analytical Application. To demonstrate that NADES fluorescence can be used for quantification purposes, the system behavior was tested in five samples of *Curcuma longa* powder. As can be seen in Figure 4, curcumin has the property to reduce the fluorescence intensity of the blue channel in NADES. It is important to point out that the whole procedure (solvent preparation and analyte extraction) was, for the first time, performed in a single step. The system was evaluated in the range between 0 and 50 mg L^{-1} of curcumin by employing the blue channel as an analytical response. The final curve was $Blue_{int} = -0.0402x$ (mg L^{-1}) + 5.2788, with a correlation coefficient of $R^2 = 0.9879$ (Figure 4, inset). This new method is very interesting from a green perspective because it saves not only time but also energy. It is important to mention that curcuminoids rapidly degrade; however, it has been demonstrated that, when they are in a mixed form, a synergistic stabilizing mechanism occurs.[29] Taking into account that the fluorometer utilized in this work is portable and could be utilized in the field, this simplification in the extraction step

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could be a very valuable approach in order to get quick results (5 min) to make decisions. Indeed, it has already been demonstrated that the interaction between curcuminoids and NADES through hydrogen bonds greatly stabilizes them.[23]

To validate the proposed one-step extraction method, the results were compared with those obtained by applying the NIST method[36] (Table 2). As can be seen, the results are similar; therefore, a *t* test for paired samples was carried out. At a 95% confidence level, the $t_{calculated}$ (1.704) was lower than the $t_{tabulated}$ value (2.776), thus indicating that there were no statistically significant differences between both methods. Additionally, the relative extraction efficiency (REE %) was calculated by employing eq 1:[38]

$$\text{relative extraction efficiency (REE \%)} = \frac{\text{percentage of curcumin extraction (single-step proposed method, g \%)}}{\text{percentage of curcumin extraction (NIST method, g \%)}} \quad (1)$$

Table 2. Obtained Results of NIST Reference Method and Single-Step Preparation–Extraction Method for Curcumin Determination[a]

sample	ref method ($\bar{x} \pm$ SD)[b]	proposed method ($\bar{x} \pm$ SD)[b]	REE %[c]
A	0.59 ± 0.05	0.58 ± 0.07	98%
B	1.43 ± 0.09	1.51 ± 0.21	106%
C	2.33 ± 0.37	2.19 ± 0.17	94%
D	3.02 ± 0.37	2.75 ± 0.41	91%
E	3.83 ± 0.26	3.45 ± 0.17	90%

[a]Experimental conditions as described in the Experimental Section. [b]$\bar{x}$ = average (g %); SD = standard deviation (g %) (n = 3). [c]REE % = relative extraction efficiency (%).

These facts demonstrate the excellent robustness and capacity of the proposed extraction, quantification, and portable detection method for curcuminoids.

Evaluation of Greenness Profile. Finally, a comparison between the proposed method and other reported works for curcumin extraction/determination was carried out (Table 3), highlighting some aspects concerning GAC. In addition, we included the AGREE score, calculated using the Analytical Greenness calculator.[33] It is a recently developed software that provides a new, complete, and easy way to evaluate analytical methods, considering all the steps, reagents, and instruments necessary to quantify an analyte. Each input criteria corresponds to one of the 12 principles of GAC, with a numerical scale assigned from 0 (red) to 1 (green), according to low or null agreement with GAC to total compliance, respectively. The software builds a pictogram with the overall score of the method in the center and the score of each criterion around it. Figure 5 shows the pictogram of the proposed method and the final score reached (0.88 points). As can be seen, an excellent punctuation was obtained, in contrast with those obtained from previous works (see Tables S2–S6 for detailed report of each work). The proposed methodology has an excellent performance in most of the Principles, which is

Table 3. Method Comparison for Curcumin Extraction[a,b]

Extraction solvent	Solvent preparation	Extractant volume	Extraction method	Sample weight/mass	Extraction time	Detection system	AGREE-Metric	Reference
CGH	Heating and stirring	10 mL	heating and stirring	0.1 g	40 min	HPLC	0.37	23
Choline chloride and lactic acid	Heating and stirring	20 mL	US probe	5 g	20 min	HPLC	0.31	24
Ethanol	-	150 mL	US probe	6 g	60 min	HPLC	0.31	25
Ethanol	-	50 mL	heating and stirring	1 g	50 min	UV-spectrophotometer	0.34	26
FCH	US probe	10 mL	US probe	0.05 g	3.40 min	Smartphone-based 3D printable device	0.88	This work

[a]CGH = citric acid–glucose (1:1), 15% water. [b]Choline chloride and lactic acid (1:1), 20% water.

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Figure 5. Pictogram report of the AGREE metric for the proposed method.

reflected in the green color. The exceptions are Principles 1, 5, and 8, where a yellow color was obtained indicating lower alignment with GAC. Principle 1 considers that it is desirable that the sample does not undergo any type of treatment before its measurement. Although our method involves an extraction step, it is carried out at the same time that the extraction solvent is prepared, marking a difference from the rest of the methods reported so far. Principles 5 and 8 could be improved with automated sample treatment and by using a multianalyte detection technique, respectively. The orange color of Principle 3 indicates that it is the worst point in our approach regarding GAC. From our point of view, the metric system could be enhanced by considering the possibility of portable devices that can make in situ measurements, avoiding the transport of the sample to the laboratory. For this reason, we decided to lessen the weight of this principle. It is important to note that a red color was not obtained in any Principle, which shows a high concordance with GAC throughout the analytical process. The proposed method provides a miniaturized pretreatment of the sample with high throughput and low waste generation. Measurements can be performed in situ through a reduced number of steps employing biodegradable reagents. Therefore, the proposed one-step methodology is an excellent option to fulfill the GAC criterion.

CONCLUSIONS AND FUTURE TRENDS

In this work, the intrinsic fluorescence of NADES is presented as a new and unexplored property. Furthermore, a brand new method for the preparation of NADES assisted by an ultrasound probe is developed and optimized, obtaining a faster and more efficient performance in comparison to heating and stirring or US bath methods. The best fluorescence properties were observed in eutectic systems formed by hydroxylated polyprotic organic acids and five-carbon monosaccharides.

This methodology allows the extraction of analytes in a single step, which was applied to curcuminoids, in *Curcuma longa*, using a portable detection system by means of a smartphone. One advantage of this procedure is the avoidance of curcuminoid degradation due to the short extraction time and the use of ultrasound cycles.

Furthermore, the greenness of this work was evaluated by employing the AGREE metric, recently reported by Pena-Pereira et al.,[33] and showed a great agreement with GAC Principles, >2.5 times greener than previously published works for curcuminoid determination. It is important to highlight that the proposed methodology allows the application of chemometric tools (to make multianalyte sensing) and the automation of the system. In this way, a greater concordance with the principles of GAC could be achieved.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.1c00406.

3D spectrum and contour 3D spectrum of FCH; fluorescence of FCH illuminated with a blacklight 365 nm UV flashlight; hydrogen-bond donor and acceptor count; rotatable bond count and topological polar surface area of tested components for NADES preparation; and Analytical Greenness report sheets (PDF)

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Notes

The authors declare no competing financial interest.

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