

**Lab in a bottle, open-source technologies for the design of affordable  
environmental samplers integrating on-site extraction**

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## ABSTRACT

Access to clean water, a Sustainable Development Goal, can only be accomplished worldwide using affordable technologies. In the analytical chemistry realm, developing cheap devices capable of on-site extraction results in a helpful tool. This article presents a new device based on open-source technologies for the on-site extraction of isoflavones from environmental waters as a proof of concept. The device is wholly operated by an Arduino microcontroller that also integrates sensors (temperature and conductivity) to provide on-site information. The extraction unit stirs into the sample, using a small motor, a planar sorptive phase consisting of Mixed-mode Anionic Exchange particles (MAX). After the on-site extraction, the sorptive phase is transported to the lab for its final analysis by liquid chromatography coupled with mass spectrometry. The analytical method provided detection limits of 1.5 ng L<sup>-1</sup> (biochanin A and formononetin) and 15 ng·L<sup>-1</sup> (daidzein and genistein). The precision, expressed as relative standard deviation, was evaluated at three concentration levels providing results better than 9.8 %. The accuracy, with relative recoveries in the 85 % to 119 % ranges, results supports the application of the method. The relevance of isotopically labeled compounds to normalize the effect of some variables on the extraction of the analytes is also discussed in detail.

*Keywords: On-site extraction; Portable; Affordable; Environmental analysis; Water samples; Phytoestrogens.*

## 1. Introduction

United Nations has established access to clean water as one of the central Sustainable Development Goals to be accomplished by 2030 [1]. The achievement of this global goal should rely on affordable technologies able to be applied everywhere, no matter the economic resources. In this context, Analytical Chemistry is responsible for providing chemical information about environmental resources, thus assessing their safety and alerting their pollution [2]. Due to the nature of environmental systems, sampling is a challenging but unavoidable step. The vast size of the systems involves a non-homogeneous distribution of the pollutants, making multi-sampling at different locations and/or times essential to fully understand the environmental problems. Although there are sensors that can be applied on-site for simple measurements [3], these devices do not cover most of the potential pollutants and have limited sensitivity. The development of miniaturized chromatographic systems coupled to portable detectors, like ion mobility, have-has opened the door to extend~~ing~~ the application scope of on-site measurement devices [4].

Passive samplers provide the average concentration of pollutants in a defined period and present a high preconcentration ability [5]. In some cases, obtaining punctual information helps to detect acute environmental problems. The classic analytical workflow in this scenario consists of sampling and transporting the sample to the laboratory. Although it is useful, this workflow faces significant challenges (e.g., maintaining the integrity of the sample until the final analysis) that may affect the analytical performance. On-site sorptive extraction appears to be a more reliable and simpler alternative. The sorptive phase (SP) stabilizes the analytes during transportation and storage since the analytes are not in contact with the aqueous matrices [6]. Also, both steps are simplified because the size of the SP is some orders of magnitude smaller than the original samples. This SP can

be quickly submitted to a central facility (e.g., a governmental laboratory) for their final analysis. This strategy allows for obtaining more information from different locations.

Sorbent-based microextraction techniques can be easily ~~on-site developed~~developed on-site. In fact, solid-phase microextraction (SPME) [7] and thin film microextraction (TFME) [8] have clearly contributed to the design of portable, miniaturized, easy-to-handle, simple, rapid, and reproducible samplers to be used in the environmental field [9–12]. Quin *et al.* designed the first device based on an electric drill where the extractant phase was attached. The drill provided agitation to the system, enhancing the transference of the analytes towards the extractant phase [13]. Since then, commercial drills have been used in other approaches, employing borosilicate disks modified with oxidized single-walled carbon nanohorns [14], nylon membranes [15] and magnetic paper [16] as extractant phases. The simplicity of microextraction techniques allows the design of special devices for sampling at difficult-to-access locations. In this sense, Grandy *et al.* proposed ~~the use of an aerial drone as~~using an aerial drone as a sampler. The drone was modified with polystyrene foam to favor its floatability, and a sorptive phase containing hydrophilic-lipophilic balance particles was used to isolate the target compounds [17]. Including affordability as a driving force in developing these devices can be considered a step forward in the transition to global science. Also, worldwide accessible and easy-to-fabricate prototypes can contribute to the so-called Citizens Science [18] being in line with the social responsibility of scientific developments [19,20]. In this context, open-source technologies can play an important role. In fact, 3D-printing elements [21,22], cell-phone based microelements [23–27], microcontrollers (Arduino, Raspberry) [28–30] or portable platforms [31] ~~has~~have been used, but scarcely, in the analytical chemistry realm.

In this article, a cost-effective device for environmental analysis is proposed. The novelty relies on the use of ~~Based on~~ open-source technologies, ~~integrating sample preparation (analyte isolation) and on-site measurement (the device allows the on-site isolation of the analytes and the on-site monitoring~~ of some physicochemical properties (temperature and conductivity) in the same device. A sorptive phase consisting of mixed-mode anionic exchange (MAX) particles is used ~~not only~~ for the extraction of the analytes. This sorptive phase, rather than the sample, is transported and stored in the laboratory until the analysis. ~~but for their stabilization during sample transportation and storage~~. These sorbents have demonstrated their potential in environmental water analysis to extract organic compounds [32,33]. Isoflavones, a group of natural phytoestrogens [34,35], were selected as model compounds. Their determination in environmental water samples is interesting due to their negative impact on the metabolism and the activity of sex hormones [36,37]. This impact results in their classification as endocrine-disrupting compounds [38].

## **2. Experimental Section**

### *2.1 Chemicals and samples.*

Methanolic standards of the analytes (biochanin A, daidzein, formononetin, and genistein; all of them purchased from Sigma-Aldrich, Madrid, Spain) and the internal standards (ISs) (daidzein-d<sub>6</sub> and genistein-d<sub>4</sub>, both from TRC Canada, Toronto, Canada) were prepared at a concentration of 1 g·L<sup>-1</sup> and stored at 4 °C. Working solutions were prepared daily by diluting the stocks in Milli-Q water (Millipore Corp., Madrid, Spain) or methanol, depending on their final use.

Oasis MAX sorbent (30 µm of particle diameter, anion- exchange capacity of 0.25 meq/g) purchased from Waters Corporation (Milford, Massachusetts, USA) was used ~~for the isolation of~~ to isolate the target analytes by a mixed-mode interaction.

Environmental water samples (fountains, an irrigation channel, private swimming pools, and a river) were obtained from different locations (Córdoba, Spain). They were collected in 2.5 L amber glass bottles and on-site extracted following the procedure described later.

### *2.2 Preparation of the magnetic MAX-based sorptive phase.*

The SP was prepared following the procedure previously described by our research group [39] with two significant changes. In this case, a support with a double area than the original one is used. This change, facilitated by designing a new extraction unit, increases the sorptive capacity of the device. Additionally, a mixed-mode anion-exchange sorbent is applied to improve the extraction of the target analytes without needing to adjust the sample pH. This change enhances the portability of the approach.

A plastic Adhesive tape strip (Supermagnete, Gottmadingen, Germany) was cut into pieces (13 x 10 mm) and used to support the extractant phase. This strip is rigid enough to avoid bending during stirring. Both faces of the tape strip were wrapped with double side adhesive tape (Milan, Mont-Ras, Spain) ~~to improve the stability of the coating~~. The ~~adapted modified strip tape~~ was introduced stirred in a vial containing MAX sorbent, and the particles adhered to the sticky surface. 6 mg of MAX was efficiently coated over the surface. Lastly, the resultant sorptive phase was agitated in an independent vessel to remove non-efficiently adhered particles. The surface of the sorptive phase was studied in a JEOL JSM 7800F microscope at the principal research facilities (SCAI) of the University of Córdoba.

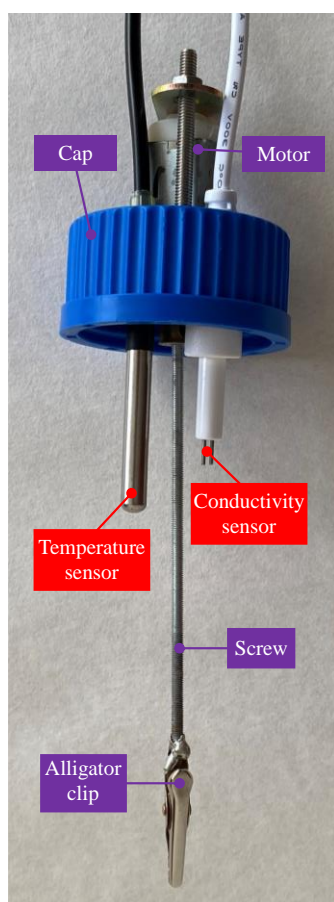
The simplicity and affordability of the preparation allow using a new sorptive phase for each extraction. Also, this procedure avoids any potential cross-contamination.

### *2.3 On-site extraction device*

A miniature electric motor (DollaTek, Hong Kong, China) is the core of the extraction device, and it is integrated into a plastic cap, as indicated in Figure 1a. This motor can

operate in the range from 3 to 6 V and it is controlled by an Arduino board. A screw (10 cm in length) is connected to the motor axis (upper side) and an alligator clip (lower side). The clip allows holding of the sorptive phase during the extraction.

To obtain physic-chemical information about the sample, Arduino technology-based temperature (SUKIKKY) and conductivity (KEYSTUDIO, Shenzhen KEYES DIY Robot co., Ltd., Shenzhen, China) sensors were used (Figure 1). The full description of the circuits and Arduino program employed is presented in the supplementary information.



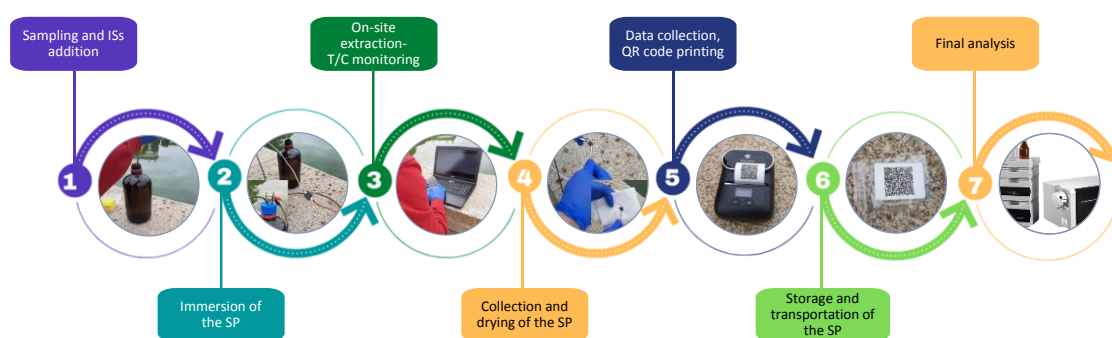
**Figure 1.** On-site extraction device integrating temperature and conductivity probes

#### 2.4 On-site extraction.

The whole on-site extraction procedure is depicted in Figure 2. Initially, 2.5 L of the unfiltered sample ~~was~~is measured using a volumetric flask and, transferred to the extraction bottle. The sample ~~was~~is fortified with the ISs ( $5 \mu\text{g}\cdot\text{L}^{-1}$ ) before the extraction.

Then, the bottle is closed with the cap (Figure 1a), thus immersing the SP and the sensors into the sample. The SP is stirred into the sample during 10 min at ca. 1500 rpm for analytes and ISSs isolation, while the conductivity and temperature are continuously monitored. After the extraction, the SP is withdrawn, dried up with a tissue, and stored in a transparent plastic bag for transportation to the laboratory. The plastic bags are labelled with a quick-response (QR) sticker that is designed in a cell phone and printed in a portable printer (Phomemo M110). The QR contains information about the samples (GPS coordinates of the sampling site, temperature, conductivity, and additional information that the operator considered relevant during the extraction) to guarantee their traceability. In the laboratory, the phases are stored at 4°C until their final analysis.

For instrumental analysis, the analytes were eluted using 500 µL of methanol containing 1 % of formic acid (v/v). For this purpose, the SP is introduced in a vial in contact with the eluent and agitated under mechanical agitation (10 min) in an orbital shaker (500 rpm) for 10 min. Finally, 5 µL of the eluate was analyzed by LC-MS/MS as described in Supplementary Material (Table S1).



**Figure 2.** Analytical procedure for the determination of isoflavones in water samples. ISSs, internal standards; SP, sorptive phase; T/C, temperature/conductivity.

### 3. Results and discussion

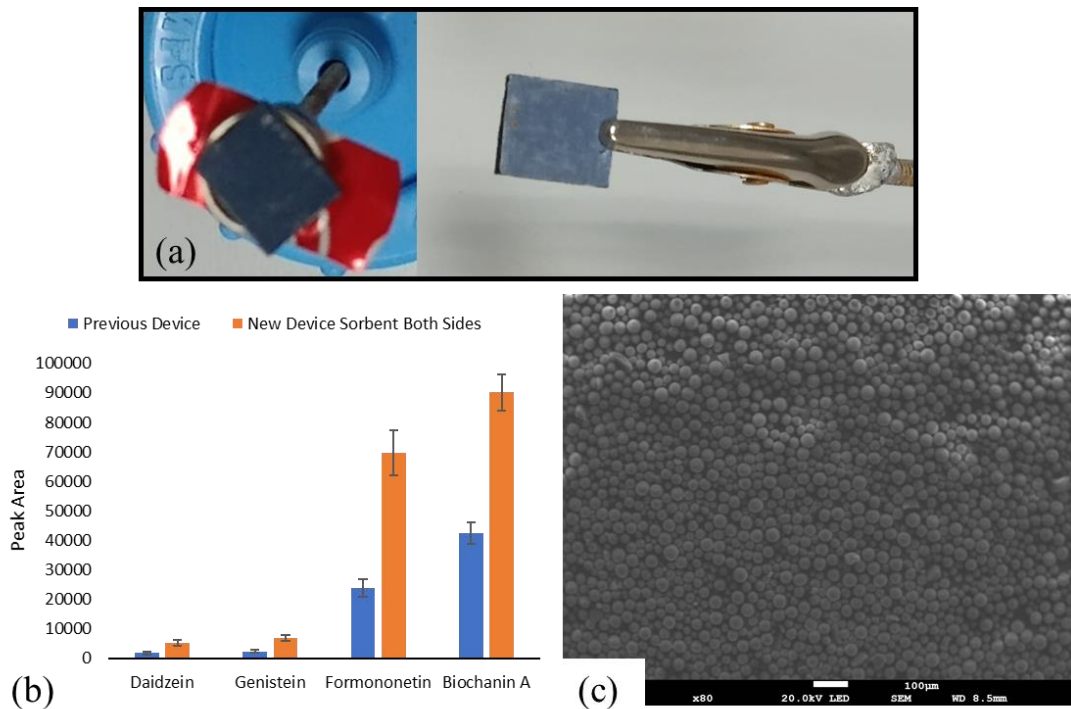
The device presented in this article results from the evolution of previously reported samplers [15,16,39] using simplicity and affordability as driving forces. Our final intention is to provide global analytical solutions sample preparation approaches that can



be implemented in any laboratory, regardless of their economic resources. The novelty of the sampler is based on four main aspects, namely: i) the integration of sensors to monitor the temperature and the conductivity of the sample; ii) the use of QR codes to guarantee the traceability of the samples from sampling to analysis; iii) the design of a new support for the sorptive phase that doubles the capacity and improves the mass transference; and iv) the application of a mixed-mode anion exchanger to promote the extraction of the phytoestrogens in the whole pH range.

Temperature (T) and conductivity were selected as parameters not only for their interest but also as an example of the extraction/measuring integrated concept. Temperature affects the partitioning of the analytes, and their monitoring during the extraction is interesting as it can vary due to sample stirring. This monitoring is especially relevant when the effect of T on the extraction is marked and IS is not available to correct the signal for a given analyte. Conductivity is used as a parameter to characterize the sample. It can be measured just once at the beginning of the extraction or monitored as it can vary with T. For brevity, ~~the two first aspects~~ sensors design ~~are entirely developed on the supplementary material describing the circuit~~ (Figures S1-S2 and Tables S2) and the QR codes (Figure S3) are entirely developed in the supplementary material.

In our previous research work, a countersunk pot magnet was used ~~as the support of to support~~ the SP [39]. This format only exposes one of the faces of the sorptive material somewhat restricting its potential capacity (Figure 3a). In this new approach, an alligator clip is used to support the phase exposing both faces of the sorptive material to the sample. This improvement is easy to observe when the analytical results obtained by each prototype are compared (Figure 3b). Also, as it has been reported for other stirring-based extraction units, the new configuration should improve the agitation of the sample [40].



**Figure 3.** (a) Comparative picture of the previous (left) and new device (right); (b) Extraction performance of the previous and the new devices; (c) SEM picture of the sorptive phase where the MAX particles are visible.

A SEM micrograph of the sorptive phase is presented in Figure 3c. The particles are distributed over the whole demonstrating the homogeneous distribution of the particles in the SP and their. ~~The size of the microparticles fits with the values reported by the supplier.~~

As it is reported, the pH of environmental waters may vary in a relatively wide interval. The pH of natural waters is typically in the 6-8 interval, while the reported values for the Guadalquivir River basin vary in the 7.7-8.2 range [41]. According to the data included in Table S3, the analytes are highly hydrophobic at pH lower than 5 ( $\log D > 2.5$ ). Due to their pKa (in the 7.75-7.85 range), while in the pH interval 6-12, they analytes are only partially ionized in the pH interval 6-8 thus reducing their logD values. Although at the normal pH for environmental waters, the non-ionized form is predominant The selection of a mixed-mode anion exchanger is relevant was selected to improve the extraction of the target analytes since it integrates hydrophobic and anion-exchange interactions. The

elution profiles (Figure S4) indicated that a fraction of the analytes (those molecules retained by reversed-phase interactions) is partially eluted with methanol while some acidic additive is needed to completely elute the compounds (including those molecules retained by a mixed mode mechanism).

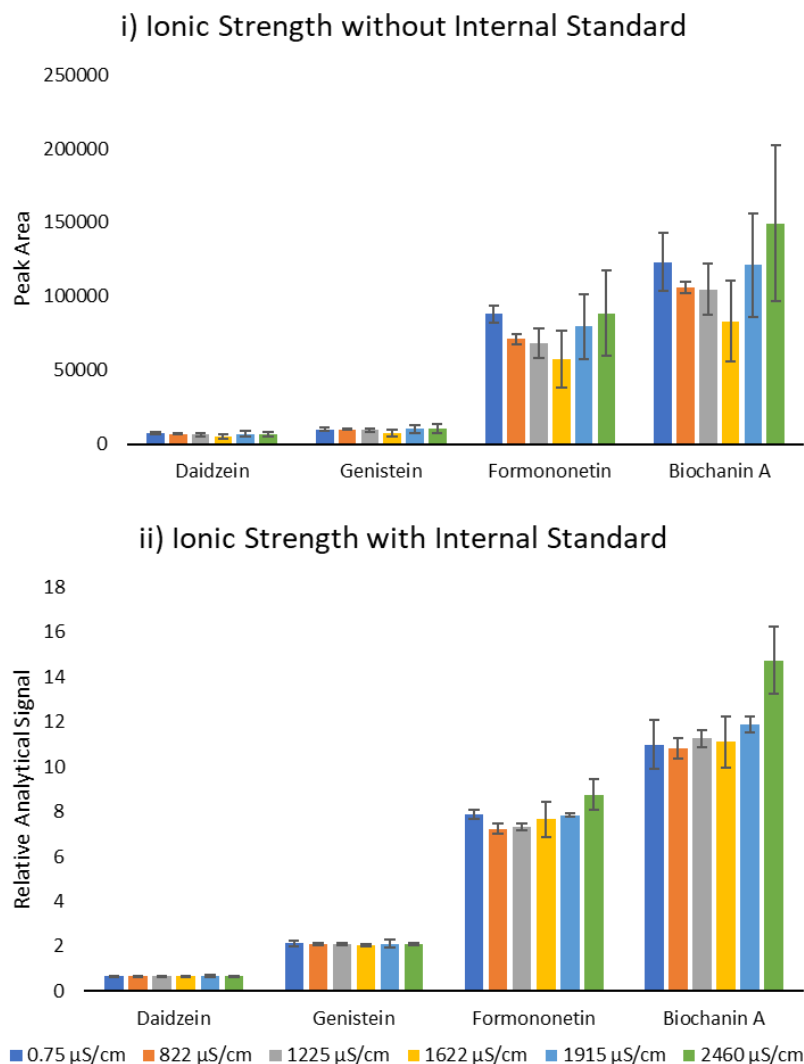
~~relative importance of each mechanism depends on the sample pH (as it is demonstrated in Figure S4).~~ The effect of the pH was evaluated in the range of 4 to 10. As is shown in

Figure S5, the differences in the analytical signal in the 6-8 interval are not significant.

For this reason, it was not necessary the pH adjustment, thus simplifying the workflow.

According to the US EPA, the conductivity of rivers in the United States usually ranges from 50 to 1500  $\mu\text{S}\cdot\text{cm}^{-1}$  [42]. For this reason, the effect of the ionic strength on the extraction of the analytes ~~were-was~~ studied in the interval from 0.75 to 2460  $\mu\text{S}\cdot\text{cm}^{-1}$  that covers the reference interval. Lower and higher values were also included to understand the effect of this chemical variable fully. The results are presented in Figure 4. Figure 4a shows the significant impact of the ionic strength on the absolute signal of the phytoestrogens. However, this effect can be neutralized by adding an adequate internal standard to the sample before its extraction, as indicated in Figure 4b. This normalization effect is evident for daidzein and genistein as they were corrected by their corresponding ISs (daidzein- $\text{d}_6$  and genistein- $\text{d}_4$ ). Due to the current unavailability in the laboratory of isotopically labelled formononetin and biochanin A, these analytes were normalized using daidzein- $\text{d}_6$  as IS. Although the precision of the measurement was lower, the ionic strength does not have a statistically significant effect in the range of 0.75 to 1915  $\mu\text{S}\cdot\text{cm}^{-1}$ .

1.



**Figure 4.** Effect of the ionic strength on the extraction of the analytes. The upper panel represents how the absolute signal varies, while the lower panel represents the evolution of the relative signal (corrected by the internal standard).

A similar effect can be observed for the extraction temperature, as discussed in the supplementary information (Figure S6).

### 3.1 Analytical characteristics of the method

The proposed on-site extraction methodology was evaluated working under the optimized conditions (Table 1). The calibration models were built using aqueous solutions of the analytes at nine concentration levels, which contain the ISs at a final concentration of  $5 \mu\text{g}\cdot\text{L}^{-1}$ . The limits of quantification (LOQ) were calculated for a S/N of 10, being in the

range from 5 ng·L<sup>-1</sup> (biochanin A and formononetin) to 50 ng·L<sup>-1</sup> (daidzein and genistein). The linearity was maintained in the interval LOQ-25000 ng·L<sup>-1</sup> with R<sup>2</sup> better than 0.9936 for all analytes. The precision expressed as relative standard deviation (RSD) was evaluated at 50, 500 and 10000 ng·L<sup>-1</sup> for five independent standards (n = 5). The RSD was lower than 9.8 %. As each extraction uses an independent SP, the RSD values also consider batch-to-batch variability.

Finally, the accuracy (% relative recovery, % RR) was evaluated by analyzing blank samples spiked at 50, 500, and 10000 ng·L<sup>-1</sup>. The results ranged from 85 % to 119 % for all the analytes. All these samples were unfiltered before being extracted, so the suspended material does not affect the extraction performance.

**Table 1.** Validation parameters of the method for the determination of phytoestrogens in waters.

Analyte	LOD (ng·L <sup>-1</sup> )	LOQ (ng·L <sup>-1</sup> )	R <sup>2</sup>	Linear range (ng·L <sup>-1</sup> )	RSD intra-day, n=5 (%)			Accuracy (% Relative Recovery)		
					50 (ng·L <sup>-1</sup> )	500 (ng·L <sup>-1</sup> )	10000 (ng·L <sup>-1</sup> )	50 (ng·L <sup>-1</sup> )	500 (ng·L <sup>-1</sup> )	10000 (ng·L <sup>-1</sup> )
Biochanin A	1.5	5.0	0.995	LOQ - 25000	2.7	9.8	6.2	99 ± 3	118 ± 12	119 ± 7
Daidzein	15	50	0.999		9.0	6.8	5.0	85 ± 8	108 ± 7	103 ± 5
Formononetin	1.5	5.0	0.994		8.5	5.4	5.4	112 ± 10	71 ± 4	90 ± 5
Genistein	15	50	0.999		8.6	5.8	3.0	99 ± 9	88 ± 5	90 ± 3

The proposed method was compared with other counterparts previously reported in the literature [43–47]. In terms of sensitivity, the new method surpasses other alternatives based on dispersive solid phase extraction, that-which are usually characterized by a high extraction efficiency [43,47]. Furthermore, the proposed method is simple, avoiding the consumption of high volumes of solvents, that those usually required in solid-solid-phase extraction [44–46]. Moreover, the main advantages of the proposal are its affordability and sustainability related with its eco-friendly characteristics and on-site application. Finally, the sustainability was evaluated using the analytical greenness metric for sample preparation tool (AGREEprep) [48]. This tool includes the whole analytical procedure,

and the final rate is not exclusive for the sample preparation step. A good score of 0.58 (Figure S7) was obtained.

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**Table 2.** Comparison of the performance of the present method with other counterparts described in the literature.

Analytes	Matrix	Pretreatment	Equipment	Sorbent (Amount (mg))	Sample volume (mL)	LOD (ng·L <sup>-1</sup> )	RSD (%)	Accuracy (%)	Reference
Biochanin A, daidzein, formononetin and genistein	River water samples	MDSPE	LC-MS/MS	Fe <sub>3</sub> O <sub>4</sub> @pDA MNPs (90)	25	1 - 20	< 6	72 - 100	[4352]
Biochanin A, daidzein, formononetin and genistein	Lake, pond, and reservoir water samples	SPE	LC-MS/MS	HLB (1000)	500	333.3 - 3333.3	< 12	63 - 124	[4453]
Biochanin A, daidzein, formononetin and genistein	Surface water samples	SPE	UHPLC-MS/MS	HLB (200 - 500)	4000	0.8 - 1	-	88.8 - 105.8	[4554]
Daidzein and genistein	Creek and river water samples	SPE	LC-MS/MS	MCX (150) HLB (150)	1000	0.8 - 2.1	4	70 - 88	[4655]
Biochanin A, daidzein, formononetin and genistein	Creek, irrigation ditch, river, swimming pool, and tap water samples	In-syringe DSPE	LC-MS/MS	Carbon fibers (30)	10	12 - 25	< 10.8	80 - 121	[4756]
Biochanin A, daidzein, formononetin and genistein	Irrigation channel, ornamental ponds, private swimming pool, and river water samples	TFME	LC-MS/MS	MAX (6)	On-site (2500)	1.5 - 15	< 9.8	85 - 119	This work

MDSPE, magnetic dispersive solid phase extraction; SPE, solid phase extraction; DSPE, dispersive solid phase extraction; TFME, thin film microextraction; LC, liquid chromatography; MS, mass spectrometry; UHPLC, ultrahigh pressure liquid chromatography; Fe<sub>3</sub>O<sub>4</sub>@pDA MNPs, magnetic nanoparticles coated with polydopamine; HLB, hydrophilic-lipophilic balance, mixed-mode anionic exchange.

### 3.2 Application to real samples

The proposed methodology was applied for the analysis of environmental water samples from different locations (fountains, [an](#) irrigation channel, private swimming pool, and [a](#) river). Table 3 shows the results obtained for the analysis of each location. [Jarošová et al. studied the concentrations reported by many studies focused on determining phytoestrogens in environmental waters \[49\]. According to these reports, phytoestrogens present concentrations below the LOD in many cases while their concentration in positive samples were in the ng per liter range.](#)

**Table 3.** Analysis of real samples.

Sample	Biochanin A (ng·L <sup>-1</sup> )	Daidzein (ng·L <sup>-1</sup> )	Formononetin (ng·L <sup>-1</sup> )	Genistein (ng·L <sup>-1</sup> )
Fountain 1	3.3 ± 0.1	-	10.9 ± 0.9	-
Fountain 2	-	-	-	-
Guadalquivir river (Location 1)	Detected	-	Detected	-
Guadalquivir river (Location 2)	Detected	-	Detected	-
Guadalquivir river (Location 3)	Detected	-	Detected	-
Irrigation channel (Location 1)	Detected	-	Detected	-
Irrigation channel (Location 2)	Detected	-	Detected	-
Swimming pool	-	-	5.9 ± 0.5	-

## 4. Conclusions

Timely and accurate chemical information is an essential pillar for protecting environmental resources. Affordability should be considered a crucial element in developing analytical strategies (including the employed devices), since it permits their worldwide application. In this article, a new device for on-site environmental extraction has been designed, having affordability as the inspirational concept. The device is cost-effective (ca. 16 €) and based on open-source technologies, thus permitting their easy reproduction. On-site extraction breaks with the classical analytical approach (based on sample transportation) and simplifies and cheapens the logistics. Also, it improves the stability of the analytes during storage, guaranteeing representativeness. The latter aspects are relevant since a single benchtop instrument (e.g., an official governmental laboratory)



can analyze samples from different locations. This aspect is particularly critical in those places where expensive instrumentation is not readily available.

The device has been evaluated using the determination of isoflavones in environmental waters as the model analytical problem. Due to the chemical characteristics of the analytes, a mixed-mode anionic exchange sorbent was used for their isolation. This selection avoids the sample pH adjustment before the extraction simplifying the overall analytical procedure. Under the optimum conditions, the analytes can be determined at very low concentrations with good precision and accuracy.

According to the results, the internal standards can play a role in normalizing the effect of ambient conditions on the extraction of the analytes. However, this normalization is only complete when isotopically labeled surrogates are used. In the research, daidzein and genistein were corrected by their corresponding deuterated surrogates. In both cases, the normalized signals (peak area of the analyte/peak area of the IS) were not affected by the ambient conditions (pH, conductivity, and temperature). Due to the current unavailability of isotopically labelled biochanin A and formononetin in the lab, these compounds were corrected using daidzein-d<sub>6</sub>. The normalized signals were not significantly affected by the sample pH and conductivity. However, the effect of the temperature (although it was studied at extreme values) was not completely corrected. We are aware that the need for ISs compounds reduces the affordability since these compounds are expensive. In the future, new alternatives (e.g., evaluating the effect of the T on the slopes of the calibration models) will be considered opening the door to using a single IS for all the analytes.

### **Credit author statement**

Francisco Antonio Casado-Carmona: Development of the prototype integrating sensors and motor, Methodology, Investigation, Data treatment, Writing.

Rafael Lucena: Conceptualization, Project organization, Writing – review & editing.

Soledad Cárdenas: Supervision, Funding acquisition, 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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