



Should we think about green or white analytical chemistry? Case study: Accelerated sample preparation using an ultrasonic bath for the simultaneous determination of Mn and Fe in beef

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ABSTRACT

Green Analytical Chemistry (GAC) metrics include a variety of criteria, such as the reagent amounts and toxicity, energy consumption, generated waste, among others. The analytical greenness metric (AGREE) and its variant for sample preparation (AGREEprep) cover different aspects that contribute to the environmental sustainability of sample preparation. White Analytical Chemistry (WAC) considers not only environmental aspects but also analytical and practical aspects with a holistic vision based on a Red-Green-Blue color model.

A case study is presented to assess the green and white profile of a method based on ultrasound-assisted extraction and determination of Mn and Fe in beef using microwave-induced plasma atomic emission spectroscopy (MP AES). The method was validated and resulted simple, fast without external heating using diluted acids.

It was concluded that we should think in green sample preparation with the AGREEprep tool, as well as in white holistic assessments (WAC) as both constitute complementary tools.

1. Introduction

Green analytical metrics are useful tools increasingly used to evaluate the environmental impact of analytical procedures employed in both industry and research. Specific metrics have been developed for Green Analytical Chemistry (GAC), such as the Analytical Eco-Scale, Green Analytical Procedure Index (GAPI), and Analytical Greenness Metric (AGREE) [1–9].

The GAC metrics help us to evaluate qualitatively and visually through pictograms how green an analytical method is. These metrics consider factors such as the quantity and toxicity of the reagents, the waste generated, energy consumption, complexity of the procedure, miniaturization, and automation. By applying these metrics, environmental impacts of analytical procedures can be identified and take actions to reduce negative effects thus contributing to more sustainable production and environmental protection [10–12].

There exist several GAC tools available, and the ideal one will depend on the specific needs or goals of the analyst or laboratory. Some popular tools include pictograms that are simple to interpret, generally with color scales from green to red [13,14]. However, it's important to note that the effectiveness of these tools may vary depending on the context and the specific metrics being measured. It's

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recommended to research and compare different tools to determine which one is best suited for an analytical method since it is not easy to find the perfect one, avoiding subjectivity. The most used green metrics generally do not fully cover what is involved in a method development that must also consider validation and once in use the quality assurance of these assays. In this sense, the approach of White Analytical Chemistry (WAC) emerges as an interesting proposal with a holistic vision [15,16]. In this metric, 12 WAC principles were proposed as an alternative to the 12 existing GAC principles introducing several criteria that affect the quality and performance of a method from an analytical (red) and practical (blue) point of view. The RGB color model, according to which the mixture of these colors would give an impression of “whiteness” brings coherence and synergy of analytical, ecological, and practical attributes of a methodology. WAC would be closer to the idea of sustainable development due to a more holistic vision, since it focuses on achieving a compromise that avoids an increase in “greenness” at the expense of functionality or quality.

Being sample preparation a critical stage in the evaluation of how green an analytical method is, an interesting metric to explore is the analytical greenness metric for sample preparation (AGREEprep) [17,18]. This GAC metric is based on 10 criteria that cover different aspects that contribute to the environmental sustainability of sample preparation.

A case study is presented to illustrate whether we should think in terms of green or white analytical chemistry. Standard methods for food analysis still recommend non-environmentally friendly procedures and the scientific community needs to understand that those methods should become obsolete [19]. Education programs in Chemistry also need to be revised to introduce GAC concepts.

The use of ultrasonic waves is a well-known option for sample preparation in food analysis [20]. Particularly, ultrasonic-assisted methods can be employed when determining essential or potentially toxic elements to assess the nutritional value of a sample or ensure food safety [21,22]. In addition, in the case of beef, these measurements can determine if the cattle require dietary supplementation [9].

There is a need for single-stage, robust, and efficient extraction methods to replace traditional procedures involving total digestion, such as microwave methods, that can be used to measure metals at highly dissimilar concentrations. Modern analytical chemists seek simple and fast methods, for which sonochemistry is an attractive strategy [22–25]. Despite the numerous reports of success using ultrasonic-assisted extraction (UAE) for the determination of mineral contents in food, these methods are still in an emerging stage and are not considered as robust or accurate as microwave-assisted methods.

Manganese and iron, two essential elements for living organisms, are found in beef in a minimum ratio of 1:160. Typical procedures for their measurement involve acid microwave-assisted digestion and subsequent analysis by atomic spectrometry. Several studies have reported the use of continuous sonication to determine only Fe in beef [26]. On the other hand, to extract several elements, a probe (20 kHz) has been employed, although this has the disadvantage of being able to prepare only one sample at a time [27].

In this case study, the use of an ultrasonic bath was explored with the aim of accelerating the sample preparation process for the simultaneous determination of Mn and Fe. These elements were selected as a challenge due to their concentration ratio in beef (1:150 or greater) to demonstrate the efficiency of an ultrasonic bath operating at 47 kHz. For this purpose, several experiments were carried out to determine the optimal conditions using dilute acids. Analytical determination was carried out by microwave-induced plasma atomic emission spectrometry (MP AES), an atomic technique that uses a nitrogen plasma and is more environmentally friendly and sustainable than other atomic spectroscopy techniques [28]. The proposed method resulted simpler and fast than microwave assisted methods. With just one step, it provides great extraction efficiency for two elements with completely different concentrations using an ultrasonic bath that is commonly found in laboratories (in industries and in universities for teaching purposes).

AGREE, AGREEprep and WAC were applied to evaluate the green and white profile of this method compared to the AOAC typical methods that use microwave-assisted digestion and concentrate acid for sample preparation and flame atomic absorption spectrometry (FAAS) for the analytical determinations [29].

A critical discussion was conducted using AGREE, AGREEprep and WAC to assess an analytical method proposed as a case study with the aim to show the weaknesses and strengths of each tool.

2. Materials and methods

2.1. Reagents

Calibration curves were prepared by serial dilution of commercial stock solutions (1000 mg L^{-1}) of Fe and Mn (Merck, Darmstadt, Germany). Concentrated HNO_3 and HCl (Merck, Darmstadt, Germany) were subjected to a sub-boiling distillation process (Milestone, Sorisole, Italy). All dilutions were gravimetrically prepared. The calibration curve ranges were 0.060–5.0 and 0.015–2.0 mg kg^{-1} for Fe and Mn, respectively. Ultrapure water ($18.2 \text{ M}\Omega \text{ cm}$ resistivity) was obtained using Millipore™ DirectQ3 UV equipment. All glassware was soaked overnight in HNO_3 (10% w/v) and then rinsed with ultrapure water.

2.2. Beef samples

Bovine muscle ERM-BB184 (provided by the Institute for Reference Materials and Measurements, European Commission, Geel, Belgium) as a certified reference material (CRM) was analyzed to evaluate figures of merit such as trueness and precision for the analytical determination of Fe and Mn. Beef samples were provided by a local slaughterhouse. This study analyzed beef from animals with an average age of 36 months (steers and heifers) and weights in the range of 109–153 kg (average of 139 kg). The selected cut corresponds to the rib plate (limited dorsally by the *M. longissimus dorsi* and ventrally by the costosternal and costochondral cartilages).

The cuts were defatted, cut into pieces, and subsequently ground with a blade mill (stainless-steel knives 440C). They were then dried at $103 \text{ }^\circ\text{C}$ (5.0 g), using an air oven until constant weight, according to the AOAC 950.46 method [30]. Once the samples were

dry, they were ground in a porcelain mortar to obtain a fine powder. Six pooled samples were obtained from twelve animals to generate a representative matrix for this study. Each pool was obtained after 5 g of dry and powdered beef from two animals was mixed and sieved.

2.3. Sample preparation procedure (UAE)

The samples were prepared using a Cole-Parmer™ 8893 ultrasonic bath (47 kHz; 230 V). The optimized procedure consisted of weighing 0.35 g of the dry sample in a 25 mL glass flask and adding a 15.00 g mixture (1:1) of $1.4 \text{ mol L}^{-1} \text{ HNO}_3$ and $1.2 \text{ mol L}^{-1} \text{ HCl}$, thus the final concentrations were $0.7 \text{ mol L}^{-1} \text{ HNO}_3$ and $0.6 \text{ mol L}^{-1} \text{ HCl}$. The flask was then placed into the ultrasonic bath for 10 min. Up to 6 flasks were simultaneously introduced in the bath (9.5 L capacity). Before the experiments, the highest point of cavitation was verified to establish the best positions to place the flasks as can be observed in Fig. 1. The test to determine the ideal position of flasks in ultrasonic baths begins by filling the tank with water. Next, a square of aluminum foil is placed in the solution for the same time of the experiment. After this, the foil should be covered with pinprick holes that are generally consistent in size and distribution; if this is observed, the bath is working effectively. In this experiment, only the upper right corner of the aluminum foil had uniform pinprick holes. Thus, the optimal position to place flasks for the extraction is shown in Fig. 1. This is a very simple and useful test for laboratory ultrasonic baths.

The obtained suspension was centrifuged for 5 min at 28,000 g, and the supernatant was used for analytical determination. All determinations for the beef samples were carried out in triplicate, and reagent blanks were also run.

The above procedure was optimized using an experimental design, two variables and three levels [31]. After optimization, the analytical method was validated according to the recommendations of the Eurachem Guide [32]. Once the method was validated, it was applied to analyze the pooled beef samples, and the results were compared with those obtained in a previous work [33].

2.4. Analytical determination

An MP AES instrument (model 4210, Agilent Technologies, Santa Clara, USA) equipped with an autosampler (model SPS 4, Agilent Technologies, Santa Clara, USA) was employed for analytical determination. The instrument was equipped with an inert One Neb nebulizer, a double-pass glass cyclonic spray chamber system, and a standard torch. The nitrogen generator (model 4107, Agilent Technologies, Santa Clara, USA) employed air by means of an air compressor (KK70 TA-200 K, Dürr Technik, Bietigheim-Bissingen, Germany).

The determinations were performed using the analytical lines at 371.993 and 403.076 nm for Fe and Mn, respectively. The plasma operation conditions were a fixed gas flow rate of 20 L min^{-1} and auxiliary gas flow rate of 1.5 L min^{-1} . For both elements, the viewing position was 0 and the nebulizer flow was 1.0 L min^{-1} .

2.5. Greenness and whiteness profile assessment

The main differences between both methods were sample preparation (ultrasonication with diluted acid vs microwave-assisted digestion with acid and peroxide) and the atomic technique used for the determinations (MP AES vs FAAS).

The two GAC metrics applied were AGREE and AGREEprep, the comparison was performed considering the standard AOAC method 999.10 [29] and the proposed method as case study (UAE). Briefly, the AOAC recommends a general procedure that is useful for the determination of several nutrients in food and is based in a microwave-assisted digestion of the sample (dry material, typically 0.5g) with concentrate HNO_3 (5 mL) and H_2O_2 (2 mL, 30 %) and subsequent determination of the metals by atomic absorption spectrometry.

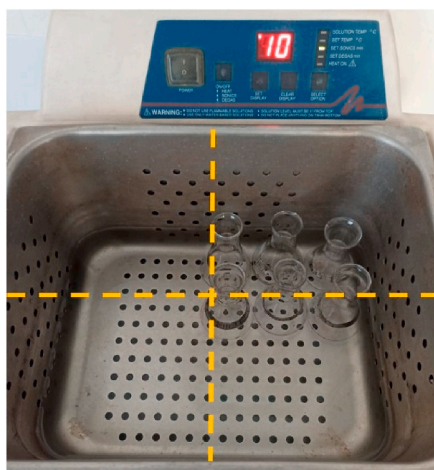


Fig. 1. Position of the sample flasks for the best performance.

In beef, Mn and Fe can be determined by Flame Atomic Absorption Spectrometry (FAAS) with an air-acetylene flame.

WAC was used according to the recommendations of Nowak et al. for the comparison of the UAE and the AOAC method [15].

3. Results and discussion

3.1. Optimization

First, the use of diluted HNO_3 (4.5 mol L^{-1}) as the extractant was evaluated since it was successfully employed to analyze beef samples treated by microwave-assisted digestion in a previous work [33]. Thus, it was interesting to evaluate if diluted HNO_3 could act as an efficient extractant in UAE for the determination of both elements in the same sample.

Table 1 shows the results of this first experimental design, where the studied variables were sonication time and HNO_3 concentration (extractant volume of 15.00 g). A CRM of bovine muscle was employed for this experiment with certified values of 75 ± 4.0 and $0.276 \pm 0.013 \text{ mg kg}^{-1}$ for Fe and Mn, respectively. The concentration ratio for this material was 1:272, which is challenging to attempt with a simultaneous extraction.

These results showed that using only HNO_3 yielded low %R for Fe. Several authors have used different strategies to improve iron extraction. Some studies have shown that more oxidative acid solution is needed to extract Fe from animal tissues and hydrogen peroxide was found necessary to improve Fe recoveries [34]. Then, a second experimental design using a mixture of HNO_3 and HCl was proposed to improve the extraction of Fe. As HCl is a well-known complexing agent for Fe, it was selected for this mixture, not in the proportions of aqua regia (1 HNO_3 : 3 HCl) but in equal parts and diluted. Table 2 presents the results of this second experimental design; the sonication time and extractant volume were not altered with respect to the first design (see Table 3).

The second experimental design resulted in a remarkable improvement in the Fe extraction with 10 min of sonication in an ultrasonic bath. After sonication, the suspension was centrifuged, and the analytical determination was carried out by MP AES. According to these results, the optimal conditions were determined as 0.35 g of the CRM and 15.00 g of extractant composed of a 0.7:0.6 mixture of HNO_3 and HCl according to the experiment 1 showed in Table 2.

After optimization, it was found that both elements could be extracted quantitatively with a sonication time of 10 min and 15 mL of a mixture of diluted HNO_3 and HCl as the extractant. Up to 6 samples were prepared at the same time after mapping the best vessel positions relative to the transducer.

3.2. Validation

After optimization, figures of merit were obtained for the proposed method according to the recommendations of the Eurachem Guide [32]. The limit of detection (LOD) and limit of quantification (LOQ) were estimated by the $3.3s$ criteria, where s is the standard deviation of the reagent blanks ($n = 10$). The linearity was studied in a suitable range considering the expected concentration levels of Fe and Mn in beef, and the precision was expressed as relative standard deviation (%RSD) using a pool of real samples. Trueness was evaluated using the bovine muscle CRM.

These results were adequate to consider the proposed method accurate for Mn and Fe determination in beef samples. Six pooled beef samples (top sirloin) were analyzed using this validated method, and the results were in the range of 0.64–0.72 and 111–121 mg kg^{-1} for Mn and Fe, respectively (dry basis). These values are in accordance with the ranges reported for the same samples in a previous work [33].

3.3. Ultrasonic bath for UAE

The use of ultrasonic baths (40–47 kHz) yields good results for extracting trace and ultra-trace elements. However, with elements present in higher concentrations, extraction with an ultrasonic bath is generally not quantitative under the same conditions. As a result, either the extractant or time must be carefully adjusted, leading to long treatment times or drastic extraction conditions. In these cases, an ultrasonic probe (20 kHz) was preferred due to its higher energy in the cavitation process [24].

Some advantages of using an ultrasonic bath instead of a probe can be highlighted. Depending on the capacity of the bath, several samples can be treated at the same time; in this case, the capacity of 9.5 L allowed for the placement of 6 vessels. Previously, the cavitation power in the cavity of the bath was studied with an aluminum sheet, thereby establishing that 6 vessels could be simultaneously treated with good precision in the results. The employed bath can contain up to 12 vessels (25 mL Erlenmeyer flasks), but

Table 1
Experimental design (three levels–two variables) using a single acid as the extractant.

Experiment	HNO_3 (mol L^{-1})	Time (min)	%R (Fe)	%R (Mn)
1	1.4	10	48	0
2	1.4	20	44	111
3	2.8	15	54	79
4	4.5	10	64	94
5	4.5	15	63	91

%R: mean recovery percentage after analysis of the bovine muscle CRM ($n = 6$ replicates of each experiment) [31].

Table 2

Experimental design (three levels–three variables) using a mixture of diluted acids as the extractant.

Experiment	HNO ₃ (mol L ⁻¹)	HCl (mol L ⁻¹)	Time (min)	%R (Fe)	%R (Mn)
1	0.7	0.6	10	82.5	108
2	0.7	0.6	20	81.5	113
3	1.4	1.2	15	83.6	114
4	2.25	2.0	10	78.9	102
5	2.25	2.0	15	70.2	105

%R: mean recovery percentage after analysis of the bovine muscle CRM ($n = 6$ replicates of each experiment) [31].

Table 3

Figures of merit of the proposed method.

Figure of merit	Fe	Mn
Linearity (studied for this application)	up to 5.0 mg L ⁻¹	up to 2.0 mg L ⁻¹
LOD (mg kg ⁻¹)	2.6	0.06
LOQ (mg kg ⁻¹)	7.7	0.19
Precision (%RSD, $n = 6$)	4.7	5.0
Trueness (%R, $n = 6$) ^a	82.5 ± 4.9	107 ± 5

^a Mean ± standard deviation; LOD: limit of detection; LOQ: limit of quantification (dry basis).

those too far from the transducer did not achieve accurate extractions for both elements. Cross contamination is also minimized using a bath as opposed to a probe.

In general, it is more likely for a laboratory to be equipped with a commercial 47 kHz ultrasonic bath than an ultrasonic probe. Thus, this method will encourage research using this instrument for mineral determination in foods even if the analytes have markedly different concentration levels. This method represents an economical alternative for food analysis that can be qualitatively considered in good agreement with the principles of GAC, since the energy consumption is considerably lower than that required by microwave-assisted digestion.

3.4. GAC metrics AGREE and AGREEprep

Before proceeding to use AGREE and AGREEprep, an additional tool was employed and adapted to this case to compare both methods to minimize a subjective opinion. For this purpose, the Chloroform-oriented Toxicity estimation Scale (ChlorTox Scale) was selected as an objective and simple approach for the evaluation of environmental and health risk, related to the use of chemical substances. The ChlorTox value is calculated by comparing the hazards of the tested substance with chloroform as standard and considering the amount of pure substance required for a single analysis. Then, the overall risk of a method is given by the sum of the ChlorTox values obtained for each reagent (Total ChlorTox), this value is related to the equivalent mass of chloroform, thus estimating the degree of risk [35].

Table 4 shows the comparison of both methodologies in terms of chemical risk evaluation using the ChlorTox Scale.

With these results in sight, two different GAC metrics AGREE and AGREEprep (Figs. 2 and 3 respectively) were employed for the proposed method (AGREE-UAE/AGREEprep-UAE) and for the comparison with the AOAC standard method (AGREE-AOAC/AGREEprep-AOAC).

It can be observed that AGREE (Fig. 2) shows a slight difference between the AOAC and the UAE methods. The differences appear due to the reduction in the amount of chemicals (acid/reagents) and energy employed comparing both procedures. This metric does not reveal the main advantages of using MP AES (multielement and with no consumption of acetylene) over FAAS.

On the other hand, the use of AGREEprep presents a significant difference between the two methods (Fig. 3). As in the previous case, the main difference between methods were the energy employed during the sample preparation and the amount of chemicals used. Even though the reasons for the differences in both methods are similar, it can be appreciated that this difference was remarkable depending on the metric employed.

Since in general terms, in this case study, the main difference between methods was the sample preparation, the use of AGREEprep was considered more adequate to present the greenness profile of the UAE, but the advantages of the use of MP AES remain masked.

Table 4

Comparison of both methods (UAE vs AOAC) in terms of ChlorTox Scale.

Method	Compound	Relative hazard (WHN)	m _{sub} (g)	ChlorTox (g)	Total ChlorTox
UAE	nitric acid	0.70	0.70	0.49	0.99
	chlorohydric acid	0.61	0.82	0.50	
AOAC	nitric acid	0.70	5.00	3.48	5.20
	hydrogen peroxide	0.26	2.00	0.52	
	acetylene	0.35	3.44	1.20	

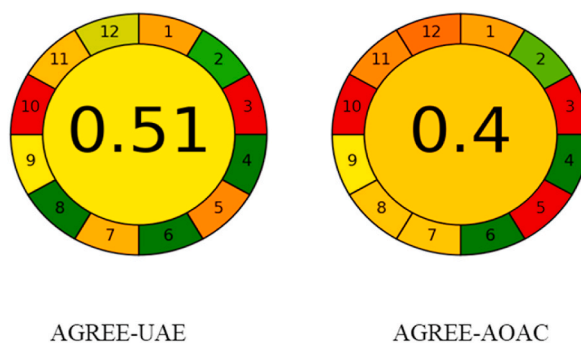


Fig. 2. Assessment results with AGREE for UAE and AOAC methods.

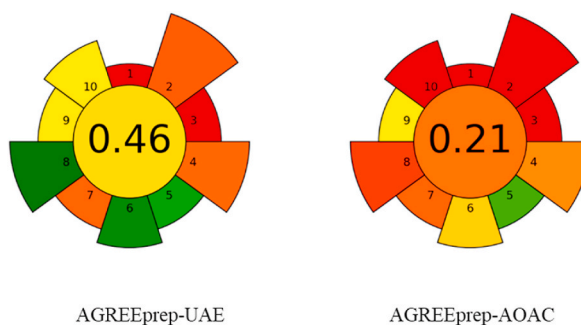


Fig. 3. Assessment results with AGREEprep for UAE and AOAC methods.

3.5. Assessment with WAC and comparison with GAC metrics

Nowadays, there are different approaches to evaluate the impact of the analytical procedures. As it was explained before, WAC proposes a tool to evaluate not only the sample preparation and technique employed, as in the GAC principles, but also, the analytical efficiency and practical/economic criteria [15]. Fig. 4 presents the results of the comparison of the UAE method vs AOAC standard method with the WAC approach. Using this tool, it can be observed that in terms of analytical efficiency (red) there was no difference between both methods. However, in terms of GAC (green) and practical/economic criteria (blue), there is an appreciable difference, thus indicating the “whiteness” of the proposed method. This holistic approach now allows us to show the advantages of the analytical technique used (MP AES), thanks to the incorporation of the “blue criteria”.

Through this case study the difference between methods in terms of sample preparation, allowed to visualize that the use of AGREE (Fig. 2), AGREEprep (Fig. 3) and WAC (Fig. 4) metrics, agree. On the other hand, WAC allows one to visualize the advantages of the analytical technique, masked in the other metrics. Finally, the UAE method for Mn and Fe determination in beef resulted to be greener and “whiter” than the standard AOAC method.

AGREEprep and WAC can be considered complementary metrics when a new sample preparation method is developed, while WAC presents an overall point of view of the methodology, AGREEprep allows to evaluate which are the critical stages from the GAC point of view.

Recently the multicriteria approach was exemplified by Novak et al. for chromatographic techniques, encouraging global assessments [36] employing algorithms that reduces the subjectivity of the greenness categorization. However, it is necessary to have simple tools to explore and to consolidate the concept of the need of studies on GAC. In general, researchers and educational fields usually consider that doing these studies is a waste of time, thus sharing case studies of different techniques can contribute to demonstrate that it is worthwhile since the long-term economic benefits and time saving are remarkable.

It is interesting also to encourage the use of these tools with specific case studies for teaching purposes including the GAC, and WAC concepts in the teaching of Analytical Chemistry in the university courses.

4. Conclusions

A case study to discuss GAC and WAC metrics was presented, for this purpose a UAE method for the determination of Mn and Fe in beef samples was developed using an ultrasonic bath. The goal of this simple sample preparation method was to determine two elements present at concentration ratios of more than 1:100. Depending on the capacity of the bath, several samples can be prepared at the same time within 10 min. This research encourages exploring the capabilities of ultrasonic baths (47 kHz), which are commonly available in laboratories. The use of dilute acids and short times for sample preparation steps make this proposed procedure greener

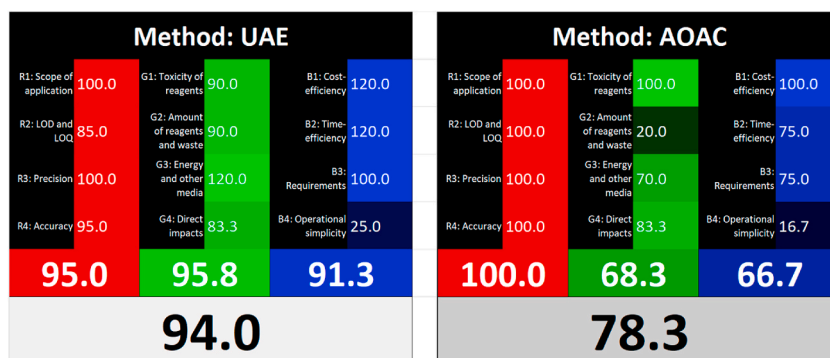


Fig. 4. Assessment results with WAC for UAE and AOAC methods.

and whiter than others used as reference methods for food analysis (classical AOAC standard methods).

The use of AGREEprep allowed to better evaluate step by step the sample preparation and helps to think in alternatives to improve it. On the other hand, the use of WAC, not only include the GAC principles, but also analytical suitability and costs showing how efficient can be the analytical technique employed, in this case MP AES which resulted in a more adequate and sustainable solution than the traditional determinations using FAAS.

Data availability

No. Data will be available on request.

CRedit authorship contribution statement

Javier Silva: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Writing – original draft, Writing – review & editing. **Valery Bühl:** Data curation, Formal analysis, Methodology, Supervision, Writing – original draft, Writing – review & editing. **Fiorella Iaquina:** Data curation, Formal analysis, Methodology, Writing – original draft, Writing – review & editing. **Mariela Pistón:** Conceptualization, Data curation, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, 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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