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Determination of the alcoholic content in whiskeys using micellar electrokinetic chromatography on microchips

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ABSTRACT

This report describes the development of a methodology based on micellar electrokinetic chromatography for the separation of alcohols on chip-based systems aiming the determination of alcoholic content in whiskey samples. The separation conditions were optimized the best results were achieved using 50 mmolL^{-1} phosphate buffer containing 30 mmolL^{-1} sodium dodecyl sulfate. The alcoholic content was determined in 16 seized whiskey samples from 4 different brands as well as in the original samples. The methodology presented herein allowed the correct classification of 75% of the seized samples as adulterated and the data obtained did not statistically differ from those recorded by a reference technique. The proposed analytical approach emerges as a promising tool to provide a rapid screening of the beverages authenticity and it may be useful to be widely explored for the quality control.

1. Introduction

Capillary electrophoresis (CE) is a powerful separation technique which has been widely used in analytical sciences (Dziomba, Ciura, Markuszewski, & Wielgomas, 2017). This separation technique has been one of the pioneering to be implemented on chip-based systems due to mainly its instrumental simplicity and other inherent advantages offered by the miniaturization as short analysis time, reduced sample consumption, high-throughput capability and portability (Castro & Manz, 2015; Wuethrich & Quirino, 2019). Microchip electrophoresis (ME) devices have been explored for a wide range of applications involving, for example, bioanalytical (Chong, Thang, Quirino, & See, 2017; Kašička, 2016), clinical (Caruso, Fresta, Siegel, Wijesinghe, & Lunte, 2017; Phillips, 2018), environmental (Freitas, Moreira, de Oliveira Tavares, & Coltro, 2016), food (Dossi, Piccin, Bontempelli, Carrilho, & Wang, 2007) and forensic studies (Verpoorte, 2007). The use of electrophoresis for forensic applications was first reported by Weinberger and Lurie in 1991, who demonstrated the analysis of illicit drugs in synthetic samples using conventional CE (Weinberger & Lurie, 1991). Since this pioneering report, many studies have explored conventional CE instruments coupled with optical or electrochemical detectors for forensic applications (Pascali, Bortolotti, & Tagliaro, 2012; Thormann et al., 1999; von Heeren & Thormann, 1997; Zaugg & Thormann, 2000).

In the last years, chip-based electrophoresis devices have emerged as powerful platforms for on-site forensic applications (de Araujo et al., 2018). When compared to conventional CE systems, the use of miniaturized devices offers attractive features like the possibility of rapid screening using portable instrumentation and the ability to provide simple yes/no answers in a matter of seconds. Some examples reporting forensic applications on chip-based electrophoresis including the separation of explosives (Piccin, Dossi, Cagan, Carrilho, & Wang, 2009), explosive residues (Pinheiro et al., 2019), explosive vapour (Taranto, Ueland, Forbes, & Blanes, 2019), DNA fragments (Aboud, Gassmann, & Mccord, 2015), screening of seized cocaine samples (Moreira et al., 2018) and alcoholic beverages authenticity (Rezende, Moreira, Lograd, Talhavini, & Coltro, 2016) have been successfully described in the literature. Whiskey is the alcoholic beverage most susceptible to be adulterated due to its global popularity, affordability and high market value. In general, the adulteration involves dilution in water or other inexpensive and low-quality alcoholic beverages that affects consequently the color intensity as well as the alcoholic concentration (Cardoso et al., 2017; Martins, Talhavini, Vieira, Zacca, & Braga, 2017). In Brazil, the federal police have reported many seizures of whiskey bottles suspiciously adulterated. Most of these apprehensions have occurred at the borders with other South America countries (Barbeira & Stradiotto, 1998; Cardoso et al., 2017).

Conventional methodologies based on ion chromatography (MacKenzie & Aylott, 2004), spectrophotometric measurements

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(Martins et al., 2017), and gas chromatography (Parker, Kelly, Sharman, Dennis, & Howieb, 1998; Rhodes, Heaton, Goodall, & Brereton, 2009) are recognized as standard approaches to investigate the authenticity of whiskeys. One of the most important parameters for investigating the authenticity of beverages refers to their alcoholic content. However, most of the conventional methods are expensive, require bulky instrumentation and make use of large sample volumes. In this way, the different groups have reported recently the development of simpler, faster, cheaper and greener methodologies including the use of non-invasive NIR and Raman spectroscopies (Nordon, Mills, Burn, Cusick, & Littlejohn, 2005), redox titrations on paper-based analytical devices (Nogueira, Lemes, Chagas, Vieira, Talhavini, Morais, & Coltro, 2019) and paper spray ionization mass spectrometry (Teodoro et al., 2017).

In this current study, we describe for the first time the development of a methodology employing micellar electrokinetic chromatography (MEKC) on microchips to determine the alcoholic content in whiskey samples. MEKC is an electrophoretic mode suitable for the separation of neutral species and its separation principle is based on the partition equilibrium of analytes between a micellar pseudo-stationary phase and the aqueous medium (Baker, 1995). Although this separation mode is popular in conventional CE systems (Fracassi, 2000), its use in chip-based electrophoresis has been barely explored. In the methodology reported herein, the separation of alcohols on electrophoresis chips based on MEKC mode was monitored through a capacitively coupled contactless conduction detection (C^4D) method. As proof-of-concept, this study shows the separation of ethanol, butanol and pentanol and the correlation of the alcoholic content in original (authentic) and seized whiskey samples. The proposed methodology has revealed great potential to be applied in the quality control of alcoholic beverages.

2. Material and methods

2.1. Chemicals

Sodium hydroxide, sodium dodecyl sulfate (SDS), sodium dibasic phosphate, ethanol, butanol and pentanol were purchased from Sigma Aldrich (St. Louis, MO, USA) and used as received. Stock solutions were prepared weekly using ultrapure water (18.2 MΩ cm) processed through a purification system (Direct-Q® 3, Millipore, Darmstadt, Germany). Prior to analysis, sample and stock solutions were filtered through nylon filters with 0.22 mm pore diameter. Subsequent dilutions were performed with ultrapure water. All experiments were performed at room temperature (23 ± 1 °C).

2.2. Instrumentation

MEKC experiments were performed on commercial glass microchips (Micronit Microfluidics B.V. (Enschede, Netherlands) containing integrated electrodes for C^4D measurements using a commercially available system (model ER455) supplied by eDAQ (Denistone East, NSW, Australia). Glass chips were received from Micronit Microfluidics B.V. (Enschede, Netherlands). Electrophoresis chips exhibited a double-T format with 100 μm of gap and a total and effective separation channel lengths of 40 and 33 mm, respectively. All channels were 100 μm wide and 10 μm deep. For contactless conductivity measurements, the detection cell was based on four sensing electrodes of platinum with tantalum adhesion layer. The distance between excitation and detection electrode was 250 μm. These two electrodes are used as working electrodes and the other pair is used as reference system for reducing the stray capacitance (Stojkovic, Schlensky, & Hauser, 2013).

2.3. Electrokinetic control

Prior to MEKC-C^4D analysis, microchannels were filled and electrokinetically preconditioned with 0.1 mmol L^{-1} NaOH solution during 10 min. Then, the microchannels were washed with ultrapure water and electrokinetically conditioned with running buffer during 10 min. Running buffer was composed of 50 mmolL^{-1} sodium phosphate dibasic and 30 mmolL^{-1} sodium dodecyl sulfate. Sample was introduced into the microchannels through gated injection mode by applying 400 and 600 V at the sample and buffer reservoirs, respectively. After filling the channels, the voltage applied to the buffer reservoir was floated for 1 s to allow the formation of a discrete sample plug. Afterwards, the potential values were established allowing the introduction of the sample zone into the separation channel for subsequent separation of analytes based on their electrophoretic mobilities.

2.4. Contactless conductivity detection

Separations were monitored through a contactless conductivity detector supplied by eDAQ (Denistone East, NSW, Australia). For this purpose, a sinusoidal wave with 1200 kHz frequency and 20 $V_{peak\text{-}to\text{-}peak}$ excitation voltage were applied to the excitation electrode. The analytical signal was recorded in the PowerChrom software version 2.7.13.

2.5. Samples

A total of 16 seized whiskey samples (4 samples of each analyzed brand) was received from the Brazilian Federal Police. In addition, 4 original (authentic) scotch whiskey samples were acquired in a local store (Goiânia, GO, Brazil). All samples were stored in the absence of light and humidity. Samples were diluted in running buffer (50%, v/v) to minimize matrix effects and possible interferences. No further treatment of samples was performed. The authenticity of original samples was certified by Instituto Nacional de Criminalística (Brasília, DF, Brazil).

3. Reference analytical method

To evaluate the accuracy of the proposed method, each authentic whiskey was also analyzed according to the standard protocol of the Ministry of Agriculture, Livestock and Supply. The official method for determining the alcoholic content in beverages consists of a prior distillation step of whiskeys by an electronic distillation equipment (model DEE, Gibertini Elettronica) followed by density measurements on a digital densimeter (model DDM 2911 plus, Rudolph Research Analytical).

4. Results and discussion

4.1. Optimization of experimental parameters

The analytical methodology based on MEKC was selected for the analysis of alcohols on microchips due to its ability to promote the separation of neutral compounds through the addition of a charged surfactant in the running buffer (Muijselaar, Otsuka, & Terabe, 1998). Initially, SDS was evaluated as surfactant for the separation of ethanol, butanol and pentanol, all of them prepared at concentration of 2% (v/v). The experiments were performed using 50 mmol L^{-1} phosphate buffer (pH = 9.0) as a running buffer with and without SDS (20 mmol L^{-1}). Fig. 1 displays two electropherograms showing the separation of the alcohols in the mentioned conditions. Each electropherogram was recorded during two consecutive injections. As can be noted, the absence of SDS in the running buffer provided the comigration of the analytes

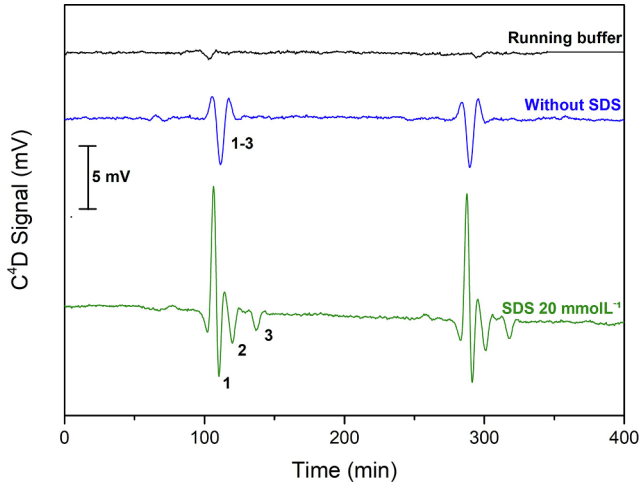

Fig. 1. Electropherograms showing the separation of (1) ethanol, (2) butanol and (3) pentanol (2% (v/v) each) in 50 mmol L^{-1} phosphate buffer (pH = 9.0) as running buffer with and without surfactant (SDS 20 mmol L^{-1}). Electrokinetic control was performed by applying of 400 and 600 V to the sampling and separation channels, respectively. Injection time (gated mode): 1 s. Detection parameters: sinusoidal wave with 1200 kHz frequency and 20 V_{pp} amplitude.

making difficult their separation. On the other hand, the addition of the surfactant enabled the separation of the alcohols due to the interaction of the analytes with the charged SDS micelles formed in the running buffer. As mentioned earlier, these micelles work as a pseudo-stationary phase and interact with the neutral analytes allowing the separation of the alcohols by polarity difference (Cheicante, Stuff, & Durst, 1995).

Since the presence of SDS above critical micellar concentration (CMC) enables the separation of alcohols with great selectivity, the SDS concentration added to the running buffer was then optimized. It is known that CMC of SDS is approximately 9.0 mmol L^{-1} at 25 °C (Deeb, Iriban, & Gust, 2011). Therefore, the SDS concentration was varied from 10 to 50 mmol L^{-1} and its effect on the separation performance was compared (Fig. 2). It is important to note that alcohols were detected as negative signals due to the conductivity difference in comparison to the running buffer. In addition, a small positive peak, characteristic of overshooting, was also observed due to the high ionic strength of the running buffer (Alves Brito-Neto, Fracassi Da Silva, Blanes, & Do Lago, 2005). This happens when MEKC is used with contactless conductivity detection due to a possible preconcentration of the surfactant prior to detection of the analyte, promoting an increase in the conductivity before the detection of the analytes. In this case, the area of the negative peak was selected for quantifying the ethanol content. Fig. S1 (available in the supplementary material) shows three electropherograms associated to the injection of sample zones containing running buffer, water and ethanol solution, previously diluted in the running buffer.

Comparing the electropherograms denoted in Fig. 2, it is clear that when SDS was added on the running buffer at concentration of 10 mmol L^{-1}, the micelles formation was not enough to allow the separation of the three analytes. On other hand, in concentrations above 20 mmol L^{-1}, the separation of the analytes was complete and the best resolution was achieved using higher concentrations of the surfactant. However, it is important to emphasize that the use of SDS at concentrations near to 50 mmol L^{-1} can generate bubbles causing noise and reducing the baseline stability. Based on that, the concentration of 30 mmol L^{-1} was chosen as the best condition, since it allowed the complete separation of three compounds within 170 s with good peak resolution ($R > 2.2$) and greatest peak relative intensity. In addition, the concentration chosen was higher than the CMC to ensure the formation of the micelles without having a large effect of overshooting or pronounced bubble formation in the system. It is well-known that pH plays an important role in the free solution electrophoretic separations, however, in MEKC the pH has a different consequence due to the micelles formation in the running buffer, being a significant parameter to be optimized. In MEKC, the micelles migrate against the electrophoretic flow, so the pH of running buffer needs to be alkaline enough to allow the separation analytes (Deeb et al., 2011). In this way, the effect of the buffer pH on the separation of alcohols was investigated using 30 mmol L^{-1} SDS. Fig. 3 displays the electropherograms recorded using running buffer solutions prepared with pH values between 7.0 and 9.0. As can be observed in Fig. 3, the separation of alcohols was complete in the three conditions, however, the highest resolution was achieved at pH 9. For this reason, this condition was selected as optimum for the subsequent experiments.

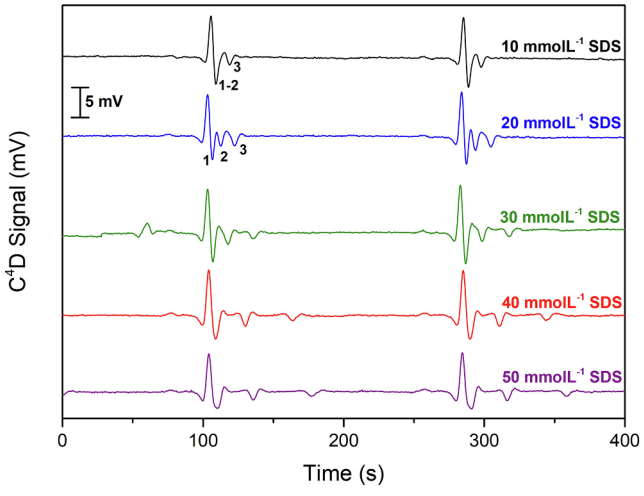

Fig. 2. Electropherograms showing the separation of (1) ethanol, (2) butanol and (3) pentanol (2% (v/v) each) in 50 mmol L^{-1} phosphate buffer (pH = 9.0) as running buffer containing different concentrations of SDS (10 to 50 mmol L^{-1}). Other conditions: see Fig. 1.

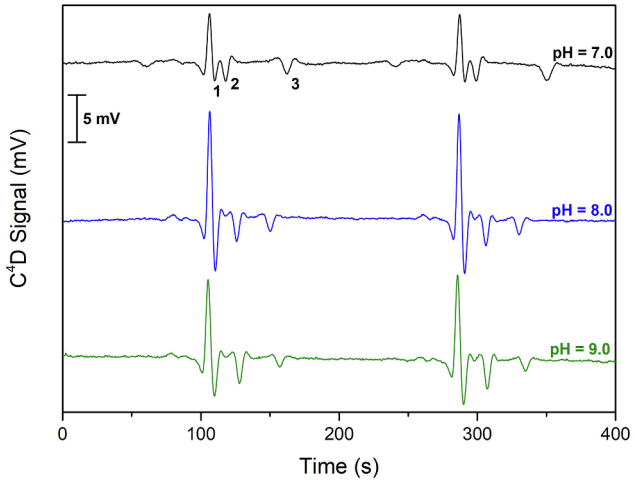

Fig. 3. Electropherograms showing the separation of (1) ethanol, (2) butanol and (3) pentanol (2% (v/v) each) in 50 mmol L^{-1} phosphate running buffer containing 30 mmol L^{-1} SDS at different pH values. Other conditions: see Fig. 1.

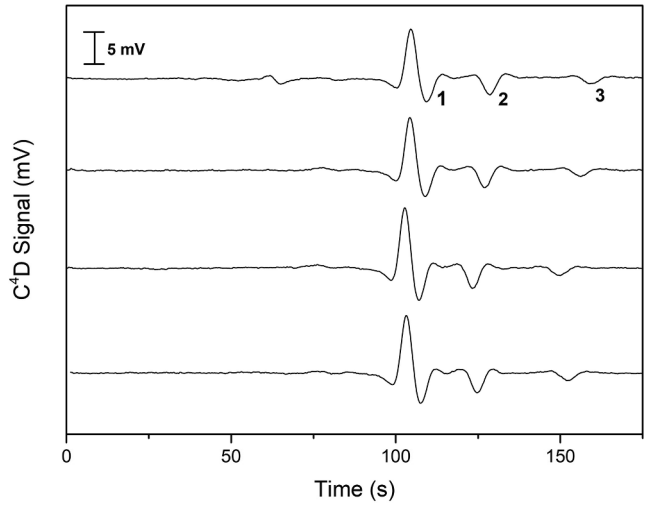

Fig. 4. Electropherograms showing the separation of successive injections of (1) ethanol, (2) butanol and (3) pentanol (2% (v/v) each) at pH = 9.0. Other experimental conditions: see Fig. 1.

4.2. Analytical performance

The analytical performance of the proposed methodology was investigated keeping constant the optimized conditions. Fig. 4 displays four electropherograms recorded sequentially showing the separation of ethanol, butanol and pentanol (2% (v/v) each). As can be noted, the separation of three compounds was completed in less than 180 s with peak-to-peak resolution greater than 1. Table 1 depicts a comparative summary of the main electrophoretic and analytical parameters achieved for each compound. In this way, the three alcohols analyzed had a good response in all parameters. The limit of detection (LOD) values (S/N = 3) achieved for ethanol, butanol and pentanol were 0.17, 0.18 and 0.50% (v/v), respectively. The LOD values achieved in our study were higher than those reported recently by other authors (Cordeiro, Ferreira Santos, Gutz, & Garcia, 2019; Santos, Da Costa, Gutz, & Garcia, 2017). However, it is important to highlight that the methodology described in this study is simpler and does not require sample treatment through electrochemical (Santos et al., 2017) or photochemical (Cordeiro et al., 2019) techniques. As mentioned earlier, the methodology adopted in this current study requires only a dilution step in the running buffer prior to analysis making is advantageous in comparison with the aforementioned reports. In addition to the LOD values, the migration time, the peak area and intensity and the efficiency obtained for each alcohol are also presented in Table 1. The proposed method revealed good linear behavior in the concentration range between 1 and 25% (v/v) and separation efficiencies from ca. 87,000 to 125,000 plates m^{-1}.

Prior to proceed the analysis of seized whiskey samples, intra and inter-day experiments were performed using authentic samples. In these experiments, quadruplicate analyzes for authentic samples were repeated for three days. The RSD values achieved for intra-day and inter-day comparisons ranged from 2.7 to 9.4% and 6.7 to 10.8%, respectively. The analytical performance of the methodology based on MEKC for the analysis of alcohols was satisfactory and the data obtained for ethanol was used to quantitatively determine the alcoholic content in whiskey samples. Considering the linear behavior in the concentration range between 1 and 25% (v/v), the only sample preparation requirement was a dilution step since whiskey samples contain a labelled alcoholic content of ca. 40%.

4.3. Analyzes of whiskeys samples

Considering the complete understanding on the separation mechanism of alcohols through MEKC mode, its application to determine the alcoholic content in 20 whiskey samples (16 seized samples plus 4 original samples) from 4 different brands (brands A-D) was then evaluated. Typical electropherograms recorded for all original and seized samples are displayed in Fig. S2 (available in the supplementary material). The authenticity of the 4 original samples, being one of each brand, was certified based on standard methodologies defined by Federal Police analyses and Ministry of Agriculture, Livestock and Supply for ethanol content in alcoholic drinks. Thus, these samples were used as a comparison parameter for the determination of alcohol content in the seized samples. Although the proposed methodology has allowed the separation of different primary alcohols, the alcoholic content was determined based on the ethanol concentration. For this purpose, the concentration was determined considering the peak area and the analytical curve (data not shown). Table 2 presents the alcoholic content labelled in the bottle (label content), the values found through the proposed methodology (experimental) and the reference method (standard) as well as the alcoholic content obtained for all the 16 seized whiskey samples by using MEKC.

As mentioned, the alcoholic content values achieved in the authentic samples were used to compare the proposed and reference methods. Based on the data presented, the results found by proposed method were similar to the concentrations achieved by the reference method, with variations between 0.8 and 3.5%. For the seized samples, the alcoholic content was compared to the value achieved in the authentic sample. The alcoholic contents obtained for the seized samples exhibited a wide variation. In some samples, the alcoholic content was ca. 8–10 times lower than the expected. The variations may be associated to the adulteration process usually employed by traffickers aiming to increase the profit through the illegal production and sales. To demonstrate the ability of the proposed method to discriminate seized from original whiskey samples, a cut off value of 10% was defined as a limit of variation. Considering this parameter, 75% of the seized samples were correctly classified as adulterated samples based on alcoholic content determined by MEKC-C^4D on microchips.

In comparison with most of the reports found in the literature, the use of MEKC-C^4D on microchips is quite advantageous in terms of sample consumption, analysis time and required instrumentation. Differently from other alternative methodologies, the separation based on the partition equilibrium makes possible the simultaneous analysis of different neutral compounds in a single run. In this way, the presented methodology has a great potential to provide a rapid screening for identifying beverage adulterations at the point-of-need.

Table 1
Comparison of electrophoretic parameters for repetitive injections of alcohols (n = 4).

Analytes	Migration time (s)	Peak intensity (mV)	Peak area (mV.s)	Efficiency (plates.m^{-1})	LOD (%, v/v)
Ethanol	108 ± 1	5.25 ± 0.67	18.67 ± 1.47	125,270 ± 16,000	0.17
Butanol	126 ± 2	3.65 ± 0.21	15.05 ± 1.26	87,660 ± 3,330	0.18
Pentanol	154 ± 4	1.33 ± 0.17	6.59 ± 0.87	108,480 ± 13,360	0.50

Table 2
Presentation and comparison of the alcoholic content (% (v/v)) found in original and seized samples of four whiskey brands (named as A, B, C and D).

Brands	Label (%, v/v)	Experimental (%, v/v)	Standard (%, v/v)	Adulterated samples value (%, v/v)			
				#1	#2	#3	#4
A	40	38.3 ± 1.2	39.7 ± 0.1	24.0 ± 0.8	35.0 ± 0.9	35.4 ± 0.7	38.9 ± 2.5
B	40	39.0 ± 1.7	39.7 ± 0.2	22.4 ± 1.3	23.5 ± 0.5	33.9 ± 0.3	6.3 ± 0.5
C	40	39.5 ± 1.7	39.7 ± 0.1	39.8 ± 2.5	34.8 ± 1.6	16.8 ± 2.2	5.0 ± 0.6
D	43	38.9 ± 0.6	39.9 ± 0.3	39.4 ± 0.2	14.2 ± 2.2	4.3 ± 0.2	39.9 ± 1.9

5. Conclusions

This study has successfully described an analytical methodology based on micellar electrokinetic chromatography on microchips to determine the alcoholic content in whiskey samples. The developed method offered short analysis time (< 180 s), linear behavior (R^2 = 0.98) in the concentration range between 1.0 and 25% (v/v) and LOD of 0.5% (v/v) for ethanol. The alcoholic content was determined in seized whiskey samples and compared to original samples previously certified. Considering the labelled alcoholic content, the achieved concentrations revealed small variation (0.8–3.5%). Using a cut off value of 10%, the reported approach was able to correctly discriminate ca. 75% of the seized whiskey samples. The developed methodology did not reveal statistical difference from the data obtained through a reference method at confidence level of 95%. Considering the achieved results, the methodology reported herein can emerge as simple and powerful strategy for the quality control of beverages as well as rapid screening tool about the authenticity of whiskey samples offering short analysis time and reduced consumption of sample.

CRediT authorship contribution statement

Kariolanda C.A. Rezende: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Writing - original draft, Writing - review & editing. **Nauyla M. Martins:** Investigation, Methodology. **Márcio Talhavini:** Investigation, Methodology. **Wendell K.T. Coltro:** Conceptualization, Funding acquisition, Project administration, Supervision, 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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