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Unmodified cellulose filter paper, a sustainable and affordable sorbent for the isolation of biogenic amines from beer samples

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ABSTRACT

While current trends in Green Analytical Chemistry aim at reducing or simplifying sample treatment, food usually comprises complex matrices where direct analysis is not possible in most cases. In this context, sample treatment plays a pivotal role. Biogenic amines are naturally formed in many foodstuffs due to the action of microorganisms, while their presence has been associated with adverse health effects. In this work, the extraction of seven biogenic amines (cadaverine, histamine, phenylethylamine, putrescine, spermidine, spermine, and tyramine) from beer samples has been simplified using laboratory filter paper as sorbent without any further modification. The analysis of the eluates by direct infusion mass spectrometry reduces the time of analysis, increasing the sample throughput. This simple but effective method enabled the determination of the analytes with limits of detection as low as 0.06 mg L^{-1} and relative standard deviations better than 11.9%. The suitability of the method has been assessed by analyzing eight different types of beers by the standard addition method.

1. Introduction

Biogenic amines (BAs) are compounds with a low molecular weight present in living organisms' cells and associated with metabolic processes [1]. They can also be detected in various foods and beverages containing free amino acids due to the action of microorganisms with decarboxylase activity and convenient circumstances for bacterial production [2]. Although BAs play an important role in different physiological activities, a high intake of these compounds may result in adverse health effects, such as headaches, arrhythmias, and alterations of blood pressure, among other consequences [3]. For this reason, the determination of BAs content in food is of high importance. Foodstuff obtained through microbial-mediated fermentation may possess high amounts of BAs, while vegetable-type foods are generally considered products with low BAs content [4]. Regarding legal limits, only histamine has been strictly restricted since it can cause so-called scombroid poisoning [5]. Depending on the fish product, the European Union has established a maximum amount of histamine of 400 mg kg^{-1} [6], while in beverages, it is recommended a concentration below 2 mg L^{-1} [7]. As for other BAs, such as cadaverine, putrescine, or spermidine, among others, no limits have been established, although ranges of 100–800 mg kg^{-1} and 30 mg kg^{-1} for tyramine and phenylethylamine, respectively, were suggested a few decades ago as safe limits [7]. Nevertheless, it is crucial to monitor the accumulation of BAs since they have a synergistic effect on the toxicological outcome of other compounds. Also, some BAs can form carcinogenic nitrosamines via interaction with nitrites [8].

Different techniques have been employed for the determination of BAs in foods and beverages, including thin-layer chromatography [9,10], capillary electrophoresis [11,12], and gas and liquid chromatography coupled to different detectors [13–16]. Among all of them, liquid chromatography (LC) coupled to mass spectrometry (MS) or ultraviolet-visible spectroscopy is the most employed. To avoid low sensitivity or tailing peaks due to the high polarity of BAs, derivatization is usually carried out [17–19]. However, this process is time-consuming and can affect the recoveries of the analytes [20]. On the other hand, food samples are complex which make sample preparation almost unavoidable.

The Green Analytical Chemistry (GAC) advocates for direct analysis, avoiding any sample preparation [21]. The recently defined White Analytical Chemistry (WAC) concept reconciles the GAC principles with the primary objective of Analytical Chemistry [22], the obtaining of reliable chemical information. Sample preparation is accepted under the WAC umbrella if it is needed to solve an

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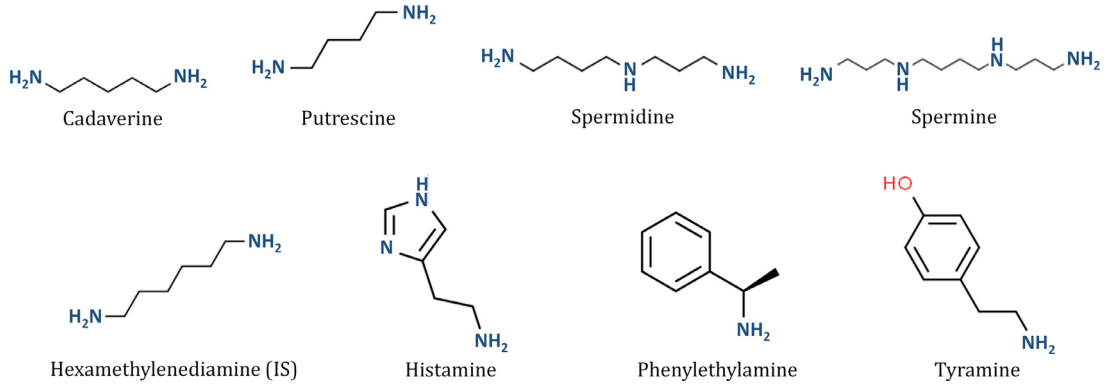

Fig. 1. Chemical structure of the biogenic amines and the internal standard employed in this work.

analytical problem. The development of efficient sample preparation procedures, which fit the analytical problem under evaluation while having a low environmental impact, can be defined as the main aim in the scenario defined by GAC and WAC. The use of natural materials in sample preparation is a clear trend [23,24]. In this context, paper has been gaining attention due to its multiple advantages. On the one hand, it is mechanically stable [25], which in turn facilitates the coupling of this material with instrumental techniques such as MS [26,27], surface-enhanced Raman spectroscopy [26,28], or fluorimetry [29]. Furthermore, it enables the spontaneous fluidic transport of compounds, reducing the amount of sample and reagents used. Also, it is a widely accessible and cost-effective material.

In this work, a fast and straightforward method for the determination of seven biogenic amines in beer samples is proposed. The analytes are isolated from the sample using unmodified cellulose filter paper as sorbent. The extraction does not require any complex apparatus since the samples are incubated with the sorbent for 45 min under continuous agitation. The analytes are quantified via direct infusion MS. The suitability of the method was evaluated by analyzing eight commercial beer samples, obtaining concentration values similar to those previously described in other works.

2. Materials and methods

2.1. Reagents

Unless otherwise specified, all reagents were obtained from Sigma-Aldrich (Madrid, Spain) with an analytical grade or better. Stock solutions of cadaverine (CAD), histamine (HIS), phenylethylamine (PHE), putrescine (PUT), spermidine (SPD), spermine (SPR) and tyramine (TYR) were prepared in HCl 0.1 mol L^{-1} at a concentration of 10,000 mg L^{-1} and stored in the dark at 4 °C. Working solutions were prepared at the appropriate concentration by dilution of the stock in HCl 0.1 mol L^{-1} or beer sample. Hexamethylenediamine (HMDA) was employed as the internal standard (IS) and was added to the sample before extraction. Fig. 1 depicts the structure of all the amines employed in this work, including the IS. During the optimization of pH and ionic strength, 1 mol L^{-1} solutions of NaOH and Na_2SO_4 were used, respectively, for the standards and sample adjustments.

Milli-Q water (Millipore Corp., Madrid, Spain), LC-MS-quality formic acid and LC-MS-quality acetonitrile were used as the carrier phase for direct infusion mass spectrometric analysis.

For the extraction of the analytes, common filter paper (i.e., Filter-Lab 42 × 52 cm, with a density of 73 g cm^{-2}) was employed as sorbent.

The different beer samples were obtained from a local market.

2.2. Extraction procedure

This research aimed to design a straightforward and rapid analytical method to determine biogenic amines in beer. For simplicity, external calibration was selected as the first approach. The standards were prepared using an aqueous media containing 5% of ethanol to mimic a conventional beer matrix. The pH and the ionic strength (expressed as electrical resistivity) were fixed at 4.34 and 7.9 10^{-4} μΩ cm, respectively. For the extraction, 1 mL of the standard, containing the IS at 1 mg L^{-1}, was placed in an Eppendorf tube and incubated with a paper strip (1.5 × 0.5 cm) for 45 min under vigorous agitation in an orbital stirrer. Later, the paper strip was rinsed with Milli-Q water for 5 min and finally eluted with 0.5 mL of a 0.1% formic acid in methanol/water 60:40 mixture for 5 min in an orbital stirrer.

As the external calibration model did not provide acceptable relative recoveries, the standard addition method was finally selected. Initially, beer samples were ultrasonically degassed. The samples were spiked with the analytes at the required concentration, adding the IS at 0.5 mg L^{-1}. Finally, the samples were extracted following the same procedure previously described for external calibration standards.

2.3. Mass spectrometry measurements

Direct infusion mass spectrometry was carried out using an Agilent 1260 Infinity HPLC system (Agilent, Palo Alto, CA, USA) arranged with an autosampler and a binary high-pressure pump. 10 μL of the standards or sample extracts were directly injected in a carrier phase composed of 0.1% formic acid in Milli-Q water (solvent A) and 0.1% formic acid in LC-MS-quality acetonitrile (solvent B) in an 85/15 v/v% proportion. The flow rate was 0.3 mL min^{-1}, and the analysis time was 2 min.

For analyte detection and quantification, an Agilent 6420 triple quadrupole MS with an electrospray source was employed. The different mass spectrometer settings were optimized to increase the selected reaction monitoring (SRM) signal. The selected values were 7 L min^{-1} flow using a temperature of 300 °C of the drying gas, i.e., nitrogen with 99.9% purity. The nebulizer pressure was kept at 30 psi, while the voltage of the capillary was set to 4000 V in positive mode. A 1 mg L^{-1} solution of standards in Milli-Q water was directly infused in the mass spectrometer to optimize the instrumental parameters for the MS/MS determination of the analytes and the IS. These parameters are specified in Table S1 (supplementary material). Finally, for data analyses, Agilent MassHunter Software (version B.06.00) was used.

3. Results and discussion

In the last years, our research group has studied in detail the design of new paper-based sorptive phases for the extraction of different analytes from food [29], biological [30,31], and environmental matrices [32]. In these materials, the paper acts as a support of the actual sorptive phase that can be a polymer [29–31], a nanoparticle [33] or a combination of both [26,32]. These coatings provide an enhancement of the sorptive capacity and or selectivity of the materials.

Metallic silver can interact selectively with amines [34]. The modification of paper with metallic silver, which can be easily developed by immersing the paper into a silver nitrate solution followed by UV curing [26], was our initial objective. However, during the first experiments, a high background extraction of the amines, in the absence of metallic silver, was observed. These results suggested the ability of unmodified paper to interact with amines. H-bonding plays a critical role in stacking cellulose chains, thus permitting their packing into fibers [35]. The disruption of the H-bonding pattern of cellulose by some amines, like ethylene diamine, has been reported [36], providing insight into the mechanism for extracting BAs from beer samples. In fact, the use of unmodified cellulose to extract amine-containing molecules can be found in the literature [37].

3.1. Evaluation of the variables that affect the extraction

The different variables that could influence the extraction efficiency and, thereby, the signal obtained in the mass spectrometry measurements, were studied following a univariate approach. Each beer sample has a characteristic ethanol content, pH, and ionic strength. For this reason, these chemical variables were evaluated in detail. The extraction kinetics was also evaluated to boost the sensitivity of the determination.

Firstly, the effect of the ethanol content was examined in the interval 0–20%. As can be observed in Fig. 2a, there are no significant differences in the range studied. However, an analysis of variance (ANOVA) was carried out to fully demonstrate this point. The results revealed that there are no significant differences ($F<F_{crit}$) in the signals in the range studied for all the analytes except for PUT, in which the F-value was slightly superior to the F_{crit}-value. Considering this result, the ethanol content was fixed at 5% for standards to mimic the beer samples matrix.

The extraction pH was studied because it affects the ionization state of both the analytes and the sorbent in solid-phase extraction procedures. The pH was studied in a range from 4.34 (lower value of the analyzed beers) to 11.5. As can be seen in Fig. 2b, the signals of SPD and HIS were positively affected by the pH. However, the signal for SPR was negatively affected at a very basic pH. For the remaining analytes (namely, CAD, PHE, PUT and TYR) no significant differences were observed in the range of pH investigated. Considering these results, a pH value of 4.34 was selected as optimum since it provided the best reproducibility while maintaining a good signal. Furthermore, all the beer samples have a similar pH value, thus avoiding further altering the matrix.

The effect of ionic strength was evaluated, using the electrical resistivity as the parameter, in the range from 18 μΩ cm (Milli-Q water) to 3.5 10^{-4} μΩ cm. As can be discerned from Fig. 3, the best results were obtained without the addition of any electrolyte to the medium. Note that the x-axis is represented in a decreasing resistivity scale since resistivity drops when the ionic strength increases. The optimum extraction condition is not realistic for sample analysis as samples present ionic strength. The electrical resistivity of several beer samples was measured, and the lower resistivity value (higher ionic strength) resulted in being 7.9 10^{-4} μΩ cm. This value was selected as the optimum as it permits the adjustment of the samples, adding an electrolyte, before their processing.

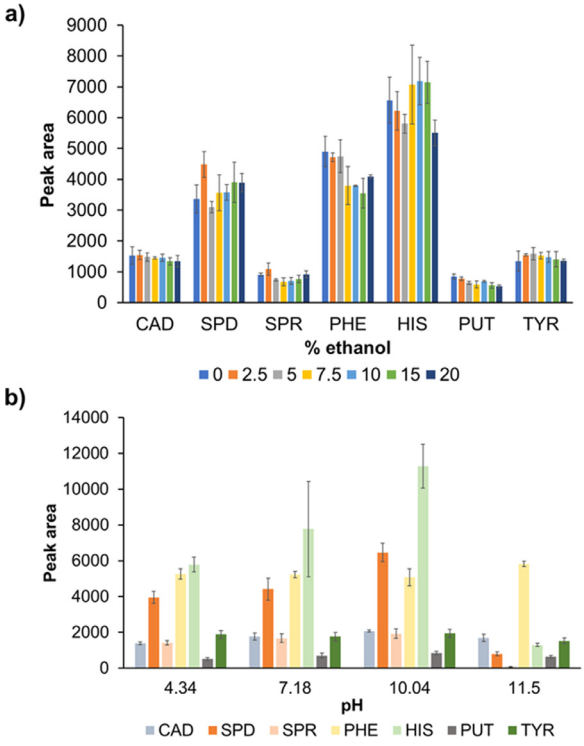

Fig. 2. Effect of (a) % of ethanol and (b) pH on the peak areas of the analytes after extraction from an aqueous solution with the analytes present at a concentration of 500 μg L^{-1}.

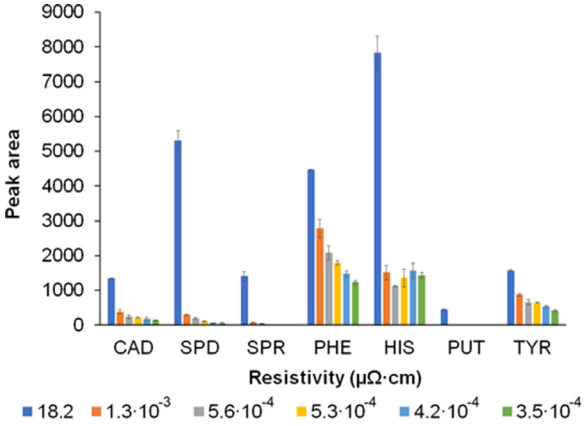

Fig. 3. Effect of the ionic strength (expressed as electrical resistivity) on the extraction of the analytes from 500 μg L^{-1} aqueous solutions.

The extraction time was studied in the range of 15–60 min. No significant differences were found in the range investigated for all the analytes except for SPD, which increases up to 45 min (Fig. S1). An analysis of variance was performed to verify this point. As expected, all the F-values were lower than the F_{crit}-values, thus confirming that there are no significant differences in the signals of the analytes in all the range studied, except for SPD in which the F-value was superior to the F_{crit}-value. Therefore, 45 min was selected as the optimal extraction time. Although it is a relatively long time, many samples can be simultaneously extracted in the orbital stirrer allowing a high sample throughput. Also, the precision values are better at 45 min compared to 15 min.

Table 1
Analytical figures of merit of the external calibration model. For building the model, solutions containing the target analytes and the internal standards were extracted, the final extracts being analyzed by direct infusion MS.

Analyte	LOD (mg L^{-1})	LOQ (mg L^{-1})	Linear range (mg L^{-1})	R^2	RSD (%)
Cadaverine	0.06	0.2	LOQ-10	0.995	9.5
Histamine	0.06	0.2	LOQ-10	0.991	6.7
Phenylethylamine	0.06	0.2	LOQ-10	0.998	0.7
Putrescine	0.18	0.6	LOQ-10	0.983	6.6
Spermidine	0.06	0.2	LOQ-10	0.990	11.9
Spermine	0.06	0.2	LOQ-10	0.996	8.6
Tyramine	0.06	0.2	LOQ-10	0.996	2.9

LOD, limit of detection; LOQ, limit of quantification; RSD, relative standard deviation.

Table 2
Analysis of beer samples by the addition standard methods. The samples were ultrasonic degassed and extracted using paper as sorptive phase. The extracts are analyzed by direct infusion MS.

Beer sample	Biogenic amine content (mg L^{-1})						
Type	% alcohol	Cadaverine	Histamine	Phenylethylamine	Putrescine	Spermidine	Spermine	Tyramine
Lager Pilsen	5	0.55 ± 0.07	< LOD	< LOD	4.47 ± 0.08	0.41 ± 0.04	> LOD < LOQ	0.66 ± 0.08
Oktoberfest-Märzen	7.2	0.9 ± 0.1	> LOD < LOQ	< LOD	6 ± 1	0.55 ± 0.05	0.39 ± 0.02	0.81 ± 0.03
Dark Lager	5.9	1.13 ± 0.03	> LOD < LOQ	< LOD	4.9 ± 0.4	0.46 ± 0.01	0.20 ± 0.01	0.93 ± 0.02
Weissbier	5	1.1 ± 0.1	0.22 ± 0.02	> LOD < LOQ	3.4 ± 0.4	1.38 ± 0.09	0.34 ± 0.02	3.7 ± 0.2
Dark abbey Belgium	6	0.62 ± 0.07	> LOD < LOQ	< LOD	Above the linear range	> LOD < LOQ	> LOD < LOQ	1.2 ± 0.2
Dark wheat beer	5.3	1.11 ± 0.08	0.27 ± 0.01	> LOD < LOQ	6.6 ± 0.7	0.46 ± 0.02	> LOD < LOQ	0.64 ± 0.04
Lager 0.0	0	1.1 ± 0.1	> LOD < LOQ	< LOD	5.2 ± 0.3	0.60 ± 0.05	0.27 ± 0.05	0.73 ± 0.09
Blond abbey	8.5	0.7 ± 0.1	> LOD < LOQ	< LOD	3.2 ± 0.3	0.22 ± 0.02	> LOD < LOQ	1.5 ± 0.2

LOD, limit of detection. LOQ, limit of quantification.

3.2. Analytical evaluation by an external calibration model

A calibration graph was built using standard solutions containing the analytes at concentrations between 0.2 and 10 mg L^{-1} and the IS at 1 mg L^{-1}. To simulate a general beer matrix, the standards contained 5% ethanol. Also, the pH and ionic strength of standards were fixed at the optimized value. The ratio (areas of the analyte)/(area of IS) was represented versus the concentration. Data were adjusted to linear models obtaining R^2 values ranging from 0.983 to 0.998. The limit of detection (LOD), obtained from a signal to noise ratio (S/N) of 3, was 0.06 mg L^{-1} for all the analytes, PUT excepted (0.18 mg L^{-1}). The limit of quantification (LOQ) for each analyte, obtained from a S/N of 10, resulted to be 0.2 mg L^{-1} for all the analytes, PUT excepted (0.6 mg L^{-1}). The precision, expressed at relative standard deviation ($n = 3$), at 2.5 mg L^{-1} varied between 0.7 and 11.9%. The data are summarized in Table 1 and the calibration graphs are shown in Fig. S2.

The application of these models to the analysis of real samples was not satisfactory since the relative recoveries were far from being quantitative. In fact, the slopes of the calibration curves obtained for standards and spiked beer samples were statistically different. For this reason, the addition standard method was selected.

3.3. Addition standard method analysis of beer samples

The reliability of the method was evaluated through the analysis of eight commercial beer samples obtained from a local market in Córdoba, Spain. The addition standard calibration graphs are shown in Fig. S3. All the analytes were detected in the eight beer samples, except for HIS and PHE, which were below the LOD in several samples. As can be observed in Table 2, CAD, PUT and TYR were the most abundant amines in all the samples, ranging from 0.55 to 1.13 mg L^{-1}, 3.25 to 15.10 mg L^{-1} and 0.64 to 3.75 mg L^{-1}, respectively.

Furthermore, SPD and SPR varied from 0.22 to 1.38 mg L^{-1} and 0.20 to 0.39 mg L^{-1}, respectively. As can be observed in Table 3, the LOQs reported in previous works for the determination of biogenic amines in food matrices are generally below the LOQs reported in this work. However, all the approaches involve chromatography and longer analysis time are required. Considering that biogenic amines are usually found at relatively high concentration levels, the previous step of chromatography has been avoided in this work and reasonable concentration levels have been obtained with direct infusion of the analytes compared to those observed in Table 3, thus demonstrating the suitability of the method for the determination of these compounds in beer samples [19,38].

4. Conclusions

In the present work, the use of common filter paper for the extraction of seven biogenic amines from beer samples and its subsequent determination via direct infusion mass spectrometry has been described. The use of paper as extracting material has multiple advantages. It is widely available and cost-effective. Its chemical structure enables its interaction with these compounds via hydrogen bonds, not requiring any chemical modification. Thus, it was possible to develop a straightforward and rapid method for the extraction of biogenic amines, a global concern due to their adverse effects on human health. The simplicity of the procedure enables the reduction of the consumption of reagents, solvents,

Table 3
Comparison of the proposed method with other counterparts proposed in the literature to determine biogenic amines in beer samples.

Biogenic amine	Sample matrix	Sample pretreatment	Extraction method	Technique	LOD (μg L^{-1})	LOQ (μg L^{-1})	Ref.
TRP, PHE, PUT, CAD, HIS, TYR, SPD and SPM	Wine and beer	Degasification, treatment with PVPP, derivatization and filtration	–	HPLC-fluorescence	30–180	200–590	[19]
PA, DMA, EA, DEA, MA, TRP, CAD, SPM, PHE, TYR, PUT, HIS, BA, HEA, isoPA, SPD and AGM	Beer	Degasification and 1 + 9 v/v dilution	–	RPLC-MS	0.54–4.30	1.6–13.0	[17]
			–	HILIC-MS	12–94	35–290	
SPM, SPD, TYR, HIS, PHE and TRP	Beer and milk	pH adjustment, filtration and derivatization (beer)	MIL-DLLME	HPLC-UV–vis	0.51–1.49	1.70–4.93	[39]
PUT, AGM, CAD, ETA, HIS, TRP, TYR and PHE	Beer	Sonication, filtration and derivatization	–	UHPLC-fluorescence	7–206	22–681	[40]
CAD, SPM, PHE, SPD, TYR, HIS, PUT and TRP	Beer	Elimination of natural biogenic amines and pH adjustment	MSPE	LC–HRMS	0.02–0.05	0.05–0.1	[41]
MA, DMA, EA, isoPPA, DEA, isoBA, MBA, PD, isoAA, MF, PP, AA, PHE, DAP, PUT, CAD, HIS and TYR	Beer	pH adjustment	DLLME	GC–MS	0.3–2.9	1.0–9.5	[42]
TYR, PHE and OCT	Beer	Derivatization	IL-UALLME	HPLC-fluorescence	0.25–50	0.83–166.67	[43]
CAD, TYR, TRP, HIS and SPD	Fermented fish, beer and wine	Sonication and filtration (beer and wine)	VSLLME	HPLC-DAD	1.0–2.6	3.3–8.5	[44]
TYR, HIS, PHE, TRP, CAD, PUT, AGM, SPD and SPM	Fermented foods, beer and wine	Sonication and filtration (beer and wine)	DUADLLME	UHPLC-MS	0.3–0.7	2–4	[45]
CAD, HIS, PHE, PUT, SPD, SPM and TYR	Beer	–	Raw filter paper	DI-MS	60–180	200–600	This work

PA: propylamine, DMA: dimethylamine, EA: ethylamine, DEA: diethylamine, MA: methylamine, TRP: tryptamine, BA: butylamine, HEA: hexylamine, isoPA: isopentylamine, AGM: agmatine, RPLC-MS: reversed phase liquid chromatography-mass spectrometry, HILIC: hydrophilic interaction liquid chromatography, MIL-DLLME: magnetic ionic liquid-dispersive liquid-liquid microextraction, PVPP: polyvinylpolypyrrolidone, ETA: ethanolamine, UHPLC: ultra-high performance liquid chromatography, MSPE: magnetic solid phase extraction, LC: liquid chromatography, isoPPA: isopropylamine, isoBA: isobutylamine, MBA: 2-methybutylamine, PD: pyrrolidine, isoAA: isoamylamine, MF: morfoline, PP: piperidine, AA: amylamine, DAP: 1,3-diaminopropane, GC: gas chromatography, OCT: octopamine, IL-UALLME: ionic liquid-based ultrasound-assisted liquid-liquid microextraction, VSLLME: vortex-assisted surfactant-enhanced emulsification liquid-liquid microextraction, DAD: diode array detector, DUADLLME: derivatization ultrasound-assisted dispersive liquid-liquid microextraction.

while paper is considered as an environmentally friendly sorbent, which keeps this method in line with the tendency of Green Analytical Chemistry. After their extraction, the analytes are measured by direct infusion mass spectrometry, reducing, even more, the analytical procedure. This strategy significantly reduces the time of analysis and sample throughput while making possible multianalyte analysis.

The use of an external calibration method for the determination of the analytes did not provide acceptable accuracy results. For this reason, the standard addition method is proposed as an alternative. This aspect can be considered as the main limitation of the approach since several standards must be prepared for the analysis of each sample. However, the possibility of the simultaneous extraction of several standards at the same time in the orbital stirrer and the rapid MS analysis (ca. 2 min) allows compensating this limitation. The applicability of the method was evaluated by analyzing eight commercial beers, in which almost all the analytes were naturally found, at concentrations similar to that obtained in previous works.

The proposed method was compared with other counterparts reported in the literature [17,19,39–45]. Our method, together with [19], is the less sensitive one, although it responds to the usual concentrations of the biogenic amines in beer samples. However, our method avoids the analyte derivatization necessary in some methods [19,39,40,43,45] and simplifies the extraction procedure compared to other approaches [41–44]. Also, the analysis time is reduced compared to those methods based on chromatographic analysis [17,19,39–45].

Declaration of Competing Interest

The authors declare that they have no competing interests or personal relationships that could have influenced in any way the work developed in this article.

CRediT authorship contribution statement

M.C. Díaz-Liñán: Investigation, Data curation, Writing - original draft. **R. Lucena:** Conceptualization, Supervision, Writing - review & editing. **S. Cárdenas:** Supervision, Funding acquisition, Writing - review & editing. **A.I. López-Lorente:** Conceptualization, Supervision, Writing - review & editing.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2021.462297.

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