Migration of dihydroxyalkylamines from polypropylene coffee capsules to Tenax® and coffee by salt-assisted liquid–liquid extraction and liquid chromatography–mass spectrometry

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Abstract

Migration of N,N-Bis(2-hydroxyethyl) alkyl(C8–C18)amines from five different polypropylene capsules to Tenax® and coffee powder have been studied. A single step extraction-cleanup procedure using salting out liquid– liquid extraction (SALLE) method followed by ultra-high performance liquid chromatography–tandem mass spectrometry (UHPLC–MS/MS) was applied. The critical parameters on the SALLE procedure such as extracting solvent, extracting volume, sample pH, salt and its concentration were optimized. The recovery values were in the range of 87.5%–106.5%. The %RSD were lower than 3.7%. The limit of detection was improved from 2.3 ng/g in Tenax® to 0.8 ng/g in coffee. The results indicated that the analyzed compounds have the potential to migrate from the polypropylene capsule containers to the coffee. In most of the cases, the migrated values were higher in Tenax® than in coffee in a range between 1.8 and 61%. One sample did not comply with the specific migration limit established by the European Commission.

Keywords:

Migration to food, LC–MS/MS, Salting-out, Polypropylene, Dihydroxyalkylamines, Coffee capsules

1. Introduction

In recent years, special attention has been focused on food safety issues due to the potential migration of high-risk chemicals from food contact materials. There are some factors such as the packaging material, the type and nature of food in contact and the storage conditions, which strongly influence the level of migrated substances (Alberto Lopes, Tsochatzis, Robouch, & Hoekstra, 2019; Nerín et al., 2013; Qian et al., 2018; Úbeda et al., 2017). Polypropylene (PP) is one of the most employed non-polar polymers, which is used to manufacture food contact materials (Simal-Gándara, Damant, & Castle, 2002; Su et al., 2019; Vera, Canellas, & Nerín, 2018). Various additives might be added to polymeric packaging materials, in order to improve their properties or facilitate the manufacturing process (Guart, Bono-Blay, Borrell, & Lacorte, 2011). These additives, particularly those with molecules and ions of small size (below 1200 Da), may be susceptible to migration from the plastic into the foodstuff (Qian et al., 2018; Simoneau, Van den Eede, & Valzacchi, 2012). In order to guarantee the safety of food packaging, the materials must fulfill the European Regulation N° 1935/ 2004 and its amendments (Parliament & Union, 2004) about materials and articles into contact with food as well as the European Regulation N° https://doi.org//10/2011/EU and its amendments (COMMISSION, 2011) focused on plastic materials in contact with food. A positive list

of additives containing their specific migration limits (SML), as well as the conditions for migration assay (temperature and simulants) are included in this Regulation. To do the specific migration studies, there are two types of methodologies; non-target and target analysis. In the first one, a screening is carried out in order to detect and identify any migrating compound, either additives or NIAS (non-intentionally added substances) that can be degradation products or impurities. While target analysis consists of detecting migrated additives intentionally added to the plastic, achieving a limit of detection enough to ensure values bellow their SMLs. Dihydroxy alkylamines are a group of tertiary amines used as antistatic agents and found in the migration from several food contact materials as polypropylene, polyethylene (PE), polystyrene (PS) and polyvinyl chloride (PVC) (Aznar, Rodriguez-Lafuente, Alfaro, & Nerin, 2012; Lierop, Castle, Feigenbaum, & Boenke, 1998; Vera et al., 2018; Vera, Canellas, Barknowitz, Goshawk, & Nerín, 2019). According to the Regulation (EC) No 10/2011 (COMMISSION, 2011), their specific migration limits correspond to 1.2 mg/kg expressed as the total sum of substances of N,N-bis(2-hydroxyethyl)alkyl (C8-C18)amines, where the difference between consecutive molecules is the gain of CH2 in their alkyl chains. For their determination, target analysis and a suitable analytical method would be required for achieving low limit of detection for the determination of total sum migration of these compounds. Chromatographic techniques along with appropriate extraction methods for determination of migrated compounds from polymer materials by exposing food or food simulants to the conventional or microwave heating and storage conditions have been widely developed (Alin & Hakkarainen, 2010; Bhunia, Sablani, Tang, & Rasco, 2013). Achieving a high recovery of analytes and overcoming matrix effects have been the important goals of sample preparation, and many sensitive methods have been developed for the determination of migration components. For instance, Lu et al. (2014) developed a LC–MS/MS coupled to SPE method to study the migration of parabens from antibacterial plastic packaging to different food simulants. Cai et al. (2017) used multi-walled carbon nanotubes (MWCNTs) in matrix solid-phase dispersion (MSPD) extraction for determination of photoinitiators and their migration into tea and milk followed by gas chromatographytandem mass spectrometry (GC–MS/MS). Li, Xu, Chen, and Xiao (2016) reported Hexafluoroisopropanol (HFIP)-induced sodium dodecylsulfate/ dodecyltrimethylammonium bromide (SDS/DTAB), a cationic surfactant coacervate extraction method coupled to high performance liquid chromatography (HPLC) and UV to determine the migration of phthalates from disposable tableware to drinking water. Shahrestani, Tehrani, Shoeibi, Aberoomand Azar, and Waqif Husain (2018) studied the comparison between different extraction methods, including liquid-liquid extraction (LLE), dispersive liquid-liquid microextraction (DLLME) and solid phase extraction (SPE), for determination of primary aromatic amines into food simulant by HPLC-UV. Recently, several authors preferred LLE techniques over SPE to extract the compounds from food samples. Salt-assisted liquid–liquid extraction (SALLE) is an alternative to LLE. During such sample treatment, the accumulation of an appropriate amount of inert salt as a salting-out reagent to the aqueous solution, enhanced the distribution ratio of analyte into the miscible organic solvent and decrease the solubility of the organic solvent in the aqueous medium, thus resulting in a twophase system (Nerin, Polo, Salafranca, & Cacho, 1996). The large surface area between the aqueous and organic phase causes acceleration of the analyte extraction. SALLE has some advantages like short time duration, low-cost, simplicity, high extraction efficiency and highly compatibility with different analytical techniques (Diuzheva, Balogh, Studenyak, Cziáky, & Jekő, 2019; Mokhtar, Abdel-Salam, & Hadad, 2019; Pasupuleti, Tsai, & Ponnusamy, 2019; Rashidipour, Heydari, Maleki, Mohammadi, & Davari, 2019).

The aim of this work was the determination of dihydroxyalkylamines concentration from five different coffee capsules. These compounds were detected after migration into Tenax® and it is very interesting to confirm if they can migrate to real coffee. To the best of our knowledge, this is the first time that the comparison of migration values to real food with migration values to dry food simulant is performed and presented. The first challenge was to develop and optimize the extraction method of migrating compounds to the coffee as a complex matrix. Salting-out assisted liquid–liquid extraction (SALLE) technique as a QuEChERS based sample preparation technique was selected for this purpose as a stable, reliable, and robust cleanup of the sample extract. Elimination of some interferences from coffee was also achieved, where a significant color removal from coffee could be observed. Several parameters including salt amount and type, pH, solvent type and amount were assessed. The migrated amounts were determined under the optimized condition by applying standard addition plots. The combination of SALLE and UHPLC–MS/MS method provided high selectivity and sensitivity that enable the quantitative analysis of coffee as a complex matrix. On the other hand, the evaluation of samples from migration into Tenax® was carried out by extracting them with a solvent and analyzing them also by UHPLC–MS/MS as it is a powerful tool for this type of analysis. Both results were compared and discussed.

2. Experimental

2.1. Chemicals and reagent

N,N-Bis(2-hydroxyethyl)dodecylamine (analytical grade), formic acid (purity > 98%) and ammonia solution 25% were purchased from Sigma-Aldrich Quimica S.A (Madrid, Spain). Methanol, acetonitrile, isopropanol (LC–MS quality), ethanol (HPLC grade), sodium Chloride (purity: 99.5%) and Sodium sulfate (purity: 99–101%) were purchased from Scharlau Chemie S.A (Sentmenat, Spain). Sodium carbonate hydrate (purity ≥ 99.0%) and ammonium bicarbonate (Bioultra ≥ 99.5%) were purchased from Sigma–Aldrich (Germany). Ammonium acetate (purity: 98%) was purchased from Merck (Darmstadt, Germany). Acetic acid (purity > 99.8%) was purchased from Fluka (Germany). Ultrapure water was produced by a Wasserlab purification system (QUGR0011; Navarra, Spain). Tenax® TA 80/100 mesh was supplied by Supelco (Bellefonde, USA). Stock solution N,NBis(2-hydroxyethyl) dodecyl amine (6000 μg g−1) was prepared in EtOH and stored in the dark at 4 °C. It was used for optimization step and preparation of the calibration curve to quantify all migrated N,N Bis(2-hydroxyethyl)(C8-C18)amines. This compound was the only one from these tertiary amines group that was commercially available. Working standard solutions were prepared daily by diluting the stock solution in water. All standards and solutions were prepared and handled under gravimetric control. Then, all concentrations were expressed as w/w.

2.2. Market samples

Five different coffee capsules manufactured with monolayer PP materials were chosen for the migration tests. They were purchased from a local supermarket in Spain and stored in the dark at room temperature. Their dimensions were 3.8 cm of diameter and 1.5 cm of height. They were from different brands and they were not closed to the expiration date when they were analyzed. Powdered coffee was used as a real food sample for the migration assays and it was bought in a local supermarket in Spain.

2.3. Optimization of SALLE procedure

As mentioned before, SALLE procedure was optimized in order to choose the best experimental conditions to extract the compounds under conditions in which they could migrate from the capsules to coffee. An optimization process started by preparing 8 g of 70 ng/g of aqueous standard solutions. Several parameters including extraction solvent, solvent volume, type and amount of salt and finally effect of pH were assessed.

2.3.1. Selection of the extraction solvent

The selection of a suitable solvent is the most crucial parameter for the SALLE method to achieve the maximum extraction efficiency. Therefore, there are some important factors that must be taken into account for choosing the solvent such as solvent polarity, density, water miscibility, its ability to be easily separated from water by adding the salt, good chromatographic behavior, property of dissolving the analytes and the nature of the sample (Rashidipour et al., 2019; Tighrine, Amir, Alfaro, Mamou, & Nerín, 2019; Zhang et al., 2019). In our study, the effects of four solvents including acetonitrile (ACN), isopropanol (IPA), methanol (MeOH) and ethanol (EtOH) were investigated for extraction.

2.3.2. Effect of solvent amount

In order to select the most appropriate organic solvent volume, six different amounts of selected solvent in the range of 1.7–3.2 g were studied.

2.3.3. Selection of salt and salt amount

Generally, in LLE methods the addition of salt to a sample solution has two objectives: 1) enhancement of the distribution of the compound into the organic phase through the salting-out effect; 2) influence of the salt into the phase separation (Otoukesh et al., 2019; Pasupuleti et al., 2019). In this work, the effect of saturated concentration of various kinds of salts including MS-friendly salting-out agents and traditional non-volatile salting-out agents, in the presence of optimized solvent, were studied (Nemeškalová et al., 2019). Sodium chloride (NaCl), sodium sulfate (Na2SO4), sodium carbonate (Na2CO3), ammonium bicarbonate (NH4HCO3) and ammonium acetate (NH4COOCH3) were chosen as salting-out agents. After that, the effect of the salt amount on extraction capacity was evaluated by adding different amounts of NH4COOCH3 in the range of 1.6–2.6 g to the sample solution.

2.3.4. Effect of pH

Due to the basic nature of dihydroxyalkylamines, the solution pH may affect their selectivity, peak shape and retention time. The effect of pH on the extraction of compound was studied at four levels by adding ammonia solution (5.0% v/v) and acetic acid (1.0% v/v) to the aqueous sample solution. The final optimized method was as follows: 8.0 g of 70.0 ng g−1 sample solution was introduced into a 12 mL centrifugal tube; 1.6 g of ammonium acetate was added into the tube. Further, the tube was sealed thereafter and vortexed for 1 min to prevent the agglomeration and to ensure sufficient interaction with the entire sample. Subsequently, 2.0 g of acetonitrile as an extraction solvent were added into the above-mentioned solution and after handshaking, the solution was centrifuged at 6000 rpm for 5 min and the organic and aqueous layers were separated during the centrifugation. The upper organic layer was collected and transferred into an auto-sampler vial for UHPLC–MS/MS analysis.

2.4. Migration assays

The migration assays were carried out with Tenax® as dry food simulant and powdered coffee as real food because the analyzed capsules were intended to be in contact with this kind of food. Previously, Tenax® was purified by Soxhlet extraction with acetone and ethanol during 6 h and further dried in the oven at 100 °C for 24 h. For the migration assays, the capsules were previously cut with a surface of 1 × 4 cm and covered with 0.16 g of Tenax® or coffee according to Regulation UNE-EN 14338 ("UNE-EN 14338, Paper and board intended to come into contact with foodstuffs – Conditions for determination of migration from paper and board using modified polyphenylene oxide (MPPO) as a simulant," 2004) (4 g Tenax®/dm2). Then, they were wrapped by an aluminum foil and placed inside of the petri dish and kept in the oven at 60 ◦C for 10 days. Three replicas of each assay and each capsule were prepared. After this step, Tenax® was extracted two consecutive times with 3 g of ethanol and concentrated under gentle stream of nitrogen up to 1.5 g and analyzed by UHPLC–MS/MS with conditions detailed below. To quantify the migration of these group of compounds, different concentration levels of N,N-Bis(2-hydroxyethyl)dodecylamine (stock solution) in ethanol were prepared. For the coffee, after migration tests, the amount of coffee was transferred to a centrifugal tube where the migrated compounds were extracted by adding 8 g of hot water (shaking for 1 min) and applying a SALLE procedure previously optimized and then analyzed by UHPLC–MS/MS under the conditions detailed below. Different concentration levels of stock solution were prepared to create the standard addition curve and besides, the relative recovery of the method was calculated for the spiked samples to check possible loss of analytes during the analytical procedure. In both cases, to calculate the migration values in ng/g, the absolute mass migrating was calculated (multiplying by 1.5 g of ethanol for Tenax® migration and 2 g of ACN for coffee migration). These values were divided by the 0.04 dm2 used in the migration test and multiplied by the ratio 0.29 dm2 of total capsule surface divided by 6.54 g of amount of coffee inside the capsule.

2.5. UHPLC–MS/MS analysis

Chromatography was carried out in an ultra-high performance liquid chromatography mass spectrometry detection equipped with triple quadrupole mass analyzer [UHPLC–MS/ MS] and the separation was done on an Acquity UHPLC BEH C18 column of 1.7 μm particle size (2.1 mm × 100 mm), both from Waters (Milford, MA, USA). Samples analysis was performed applying Mass Lynx v.4.1 software (Waters). The SIR mode was selected for the acquisition. An electrospray interface (ESI) was used as an API source (atmospheric pressure ionization) to couple the Acquity™ system to the mass analyzer supplied by Waters (TQ detector, Acquity™ Ultra Performance LC, Milford; MA, USA). The column flow rate was 0.3 mL/min and the column temperature was 40 °C. The injection volume was 10 μL under the positive electrospray interface (ESI+) mode. The MS parameters were as follows: cone voltage of 25 V for (ESI+), the capillary voltage of 3.50 KV and source temperature of 140 °C. The desolvation gas temperature (°C) and the desolvation gas flow (L h−1) both were 450. The solvents used as mobile phase A and B, were methanol and water both with 0.1% formic acid, respectively. The segmented gradient used here was constant 30% mobile phase A in 1 min and then increased gradually to 100% in 4 min and held constantly until 10 min, then reduced gradually to 30% for 10.10 min and held constantly until 12 min. The identification of homolog compounds was carried out previously (Vera et al., 2018, 2019) by UHPLC-QTOF-MSE. In this case, the retention time and the mass spectrum of the compounds were compared with the pure standard of N, N-bis (2-hydroxyethyl) dodecylamine, which was commercially available. Table 1 shows the masses and the retention times used for each studied N, N-bis (2-hydroxyethyl) amine (C8-C18).

3. Results and discussion

The migration of five different capsules for coffee has been studied in a target analysis in order to determine the amount of migrated N,NBis(2-hydroxyethyl)(C8-C18)amines . For this purpose, food simulant and real food were tested (Tenax® as dry food simulant and powder coffee). Previously, an optimization of SALLE procedure was carried out in order to choose the best experimental conditions to extract the compounds from the coffee after migration assays. After that, the migration values of food simulant and real food were compared and checked if they comply with the Regulation 10/2011.

3.1. Optimization of SALLE procedure

3.1.1. Selection of the extraction solvent

The effects of four solvents including acetonitrile (ACN), isopropanol (IPA), methanol and ethanol were investigated for extraction. The experimental results indicated that methanol and ethanol were unable to form a binary system after addition of salt as a phase separator reagent and they remained soluble in water. Acetonitrile and isopropanol had poor solubility in water due to the salting-out effect and showed good phase separation and higher extraction properties. Fig. 1a shows the obtained area for N,N-Bis(2-hydroxyethyl)dodecylamine after extraction with ACN and IPA and analyzed by UHPLC–MS/MS. The graph indicates that acetonitrile provided better results than isopropanol. This phenomenon was probably attributed to the low polarity (Log P = 4.5) and basic nature of target compounds, which made them more likely to be allocated in the polar aprotic solvent. Hence, ACN was chosen as the best organic phase for subsequent studies.

3.1.2. Effect of solvent volume

Fig. 1b shows the area response obtained for N,N-Bis(2-hydroxyethyl) dodecylamine after extraction with different volumes of C. AN and analyzed by UHPLC–MS/MS. The results indicate that by increasing the volume of solvent, the analytical signal of target analyte gradually decreased. As expected, with higher amounts of acetonitrile, the volume of the collected phase increased but it also led to a dilution of the analyte and insufficient extraction. Lower amount of solvent resulted in difficulty in separation of organic phase. According to the figure, the maximum peak area was achieved at 1.7 g of ACN which was also supported by the green chemistry requirement of utilizing fewer amounts of organic solvents. Therefore, this volume was selected for further experiments.

3.1.3. Selection of salt and salt amount

Fig. 2a shows the analytical signal of N,N-Bis(2-hydroxyethyl)dodecylamine after adding different salting-out agents including sodium chloride, sodium sulfate, sodium carbonate, ammonium bicarbonate and ammonium acetate analyzed by UHPLC–MS/MS. It was found that NH4COOCH3 had remarkable extraction capacities for this compound compared to the other salts. It should be noted that increment of the surface tension of water under the influence of salt leads to salting-out effect. Thus, salts that favor salting-out effect dramatically increase the surface tension of water. The increment in surface tension of water by salt follows the Hofmeister series (Parsegian, 1995). According to the Hofmeister series ammonium is the best cation for salting-out effect and the acetate anion is the third best anion that produces the salting-out effect. On the other hand, ammonium acetate is a non-volatile salting out agent. Therefore, MS friendly organic ammonium salt (NH4COOCH3) was chosen as a suitable salt for further studies. The effect of the salt amount on extraction capacity was evaluated by adding different amounts of NH4COOCH3 ranged from 1.6 to 2.6 g to the sample solution. According to the obtained

results given in Fig. 2b, the peak areas of analyte decreased by increasing the amount of salt. This result comes from the hygroscopic character of ammonium acetate which leads to higher water amount of the organic phase and at the same time less water retained in the aqueous phase (Fu, Song, Yi, & Xie,2019). Therefore, although the addition of salt caused an increase of sample viscosity, the organic phase volume also increased. This phenomenon led to reduction in analyte transferring and analyte dilution (Rashidipour et al., 2019). Since the separation of two phases was better in salting-out method, 1.6 g ammonium acetate was chosen as the optimal condition of salt for the subsequent steps.

3.1.4. Effect of pH

According to the obtained results given in Fig. 3, the peak areas of analyte reached its respective maxima at pH 5.0 and then were stable under the alkali and neutral conditions. It should be also considered that the pH value of coffee solution was between 5 and 6. Therefore, Ph 5.0 was chosen for the subsequent experiments.

3.2. Validation of method

The validation of the proposed analytical method was performed according to limit of detection, limit of quantification, linearity, repeatability and accuracy through recovery assays. In this regard, limit of detection (LOD) was calculated based on three times the signal to noise ratio (3:1) and limit of quantification (LOQ) was equal to ten times the signal to noise level (10:1). These parameters were evaluated by preparing the calibration curve at different concentrations of N,N-Bis (2-hydroxyethyl)dodecylamine in water and ethanol and then applying the SALLE procedure. The first calibration curve was used to quantify the migration to coffee, and the second one, to calculate the migration to Tenax®. Good results in terms of LOD and LOQ are shown in Table 2a. LOD was 2.3 ± 0.3 ng/g in ethanol and 0.8 ± 0.2 ng/g in water. The linearity concentration ranges of the method were from 10.6 to 860 ng/g in ethanol and 2.7 to 106.0 ng/g in water and the calibration curves fitted to a linear regression model with $r = 0.9986$ and $r = 0.9950$, respectively. The precision of the method was evaluated in terms of repeatability and expressed as relative standard deviation (RSD%). The RSD% was obtained by analyzing the samples in optimized conditions, using three replicates and three points of calibration curve at 5, 45 and 90 ng/g. The RSD% results were 2.4, 1.1 and 0.5 in ethanol and 3.7, 0.7 and 0.3 in water, respectively. The accuracy and effectiveness of the method applied to coffee was determined based on the average relative recovery values. Recovery studies were conducted after optimization at three concentrations levels by spiking the coffee samples. A standard addition calibration curve and subtracting the blank value was utilized to quantify the average recoveries. Satisfactory results were obtained in the range of 87.5–106.5%. The results are presented in Table 2b.

3.3. Migration studies

As mentioned above, the migration was carried out in both Tenax® as dry food simulant and in coffee as real food. The migration results are shown in Table 3. Among all studied N,N-Bis(2-hydroxyethyl)alkylamines, only C12, C13 and C15 amines migrated to the coffee or/and Tenax®. This fact is in good agreement with the previous works (Aznar et al., 2012; Vera et al., 2018, 2019) where these amines were the most common ones found in the migration assays from different materials into different simulants. The rest of analytes were below LOD that correspond to 3.8 μg/Kg and 1.77 μg/Kg for Tenax® and coffee, respectively (taking into account the LOD obtained and the calculations presented in paragraph 2.4). The highest values of migration were found for C13 amine and were 44.3–1310 μg/kg for Tenax® and 40–1050 μg/kg for coffee. Comparing the migration values for both Tenax® and coffee, in most of the cases, they were higher for Tenax®

than for coffee in a range between 1.8 and 61%. This fact could be explained by the high absorbing capacity of Tenax®. It should be highlighted that the obtained results are very valuable because they show that migration into Tenax® gives, as expected, overestimated results in comparison to the real food. It is desirable behavior because it makes Tenax® a suitable simulant in terms of food safety. No previous demonstration of migration to coffee from PP capsules has been published. When comparing the samples, it can be seen that in the capsule 3 the highest values of migration were obtained, where the total specific migration concentration of dihydroxyalkylamines exceeded the overall concentration recommended by the European Commission (1.2 mg per kg of food) (COMMISSION, 2011) for both Tenax® and coffee.

4. Conclusion

The migration of N,N-Bis(2-hydroxyethyl)(C8-C18)amines compounds from five different capsules of coffee has been studied. This study has been performed using food simulant and real food (Tenax® as dry food simulant and powdered coffee as real food) and they have been analyzed using UHPLC–MS/MS. Previously, SALLE procedure was optimized in order to choose the best experimental conditions to extract the compounds from the coffee samples. According to the results, SALLE coupled to UHPLC–MS/MS is an efficient method for clean-up of samples and analysis of compounds migrated to the coffee. Compound recoveries in the range of 87.5–106.5% with good repeatability have been obtained for the method. Also, the limit of detection and quantification were improved without significant interfering peaks from the coffee matrix, that may interfere with the analytes during the study. Besides, relatively clean extracts were obtained without requiring expensive SPE columns or evaporation and reconstitution steps. Ammonium acetate was used as a MS-friendly salting-out agent and thus, the potentially harmful effect of inorganic salts on MS systems was avoided. In the case of migration study, the results have demonstrated that among all analyzed compounds only C12, C13 and C15 amines could migrate to the coffee. Higher values of migration to Tenax® than to coffee were obtained in a range between 1.8 and 61%, demonstrating the overestimation in terms of migration for Tenax® as food simulant. Finally, one of the capsules exceeded the overall concentration recommended by the European Commission (1.2 mg per kg of food) (COMMISSION, 2011) both for Tenax® and coffee.

CRediT authorship contribution statement

Mahdiyeh Otoukesh: Validation. Paula Vera: Validation, Supervision, Writing - original draft. Magdalena Wrona: Validation. Cristina Nerin: Supervision, Writing - review & editing. Zarrin Es'haghi: Supervision.

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Tables and Figures

Table 1: N,N-Bis(2-hydroxyethyl) alkyl amines studied, their codes used, CAS numbers, molecular formulas, retention time and their characteristic masses by UHPLC–MS/MS.

Compound	Code	CAS number	Molecular formula	t_r (min)	SIR masses $[MH^+]$	Daughter masses
N,N-Bis(2-hydroxyethyl)octylamine	C8amine	15520-05-5	$C_{12}H_{27}NO_2$	3.32	218.2	200.2
N,N-Bis(2-hydroxyethyl) decylamine	C10amine	18924-65-7	$C_{14}H_{31}NO_2$	4.47	246.2	228.2
N,N-Bis(2-hydroxyethyl) dodecylamine	C12amine	1541-67-9	$C_{16}H_{35}NO_2$	5.42	274.2	256.2
N,N-Bis(2-hydroxyethyl) trydecylamine	C13amine	18312-57-7	$C_{17}H_{37}NO_2$	5.58	288.3	270.2
N,N-Bis(2-hydroxyethyl) tetradecylamine	C14amine	18927-66-8	$C_{18}H_{39}NO_2$	6.29	302.3	284.3
N,N-Bis(2-hydroxyethyl) pentadecylamine	C15amine	24910-32-5	$C_{19}H_{41}NO_2$	6.42	316.3	298.3
N,N-Bis(2-hydroxyethyl) hexadecylamine	C16amine	18924-67-9	$C_{20}H_{43}NO_2$	6.59	330.3	312.3
N,N-Bis(2-hydroxyethyl) octadecylamine	C18amine	10213-78-2	$C_{22}H_{47}NO_2$	6.72	358.3	340.3

Table 2a: Analytical parameters of the UHPLC–MS-MS method.

Compound	Calibration	Equation	r	LOD (ng/g)	LOQ (ng/g)	Linear range (ng/g)
N,N-Bis(2-hydroxyethyl)dodecylamine	Calibrate curve in ethanol	Y = 187455 + 324592	0.9986	2.3 ± 0.3	10.6 ± 1.3	10.6–860
N,N-Bis(2-hydroxyethyl)dodecylamine	Calibrate curve in water after SALLE procedure	y = 75917x − 535,379	0.9950	0.8 ± 0.2	2.7 ± 0.7	2.7–106

Table 2b
Average relative recovery percent (RR%) and concentration of N,N-Bis(2-hydroxyethyl) dodecylamine in coffee sample.

Spiked level (ng/g)	Found (ng/g)	Average RR% (n = 3)	RSD% (n = 3)
–	10.1 ± 0.3	–	2.8%
16	27.7 ± 0.3	106.5%	1.7%
49	53.2 ± 1.2	87.5%	2.7%
80	82.1 ± 3.5	87.9	4.9%

Table 3: Migration concentrations expressed as µg/kg of dihydroxy alkylamines from 5 different capsules to coffee samples and Tenax.

Sample	Migration concentration(µg/kg)					
	To Tenax			To Coffee		
	$C_{12amine}$	$C_{13amine}$	$C_{15amine}$	$C_{12amine}$	$C_{13amine}$	$C_{15amine}$
Capsule1	41.3 ± 1.7	225 ± 5	117 ± 7	29.5 ± 1.1	180 ± 2	75.2 ± 0.6
Capsule2	35.2 ± 0.6	501 ± 40	165 ± 8	31.8 ± 1.8	492 ± 21	153 ± 1
Capsule3	463 ± 9	1310 ± 97	155 ± 3	425 ± 4	1050 ± 14	201 ± 2
Capsule4	35.1 ± 0.9	44.3 ± 0.9	33.8 ± 1.6	31.9 ± 1.3	40.0 ± 1.9	34.2 ± 1.0
Capsule5	39.2 ± 0.6	306 ± 18	96.1 ± 4.8	28.3 ± 1.4	189 ± 6	83.9 ± 3.7

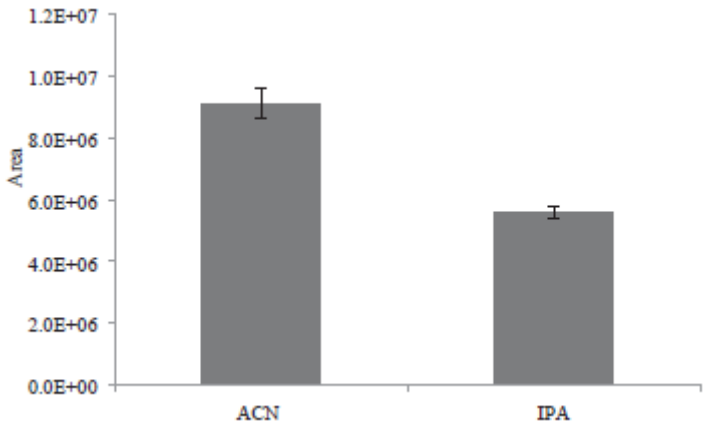

Fig. 1a. Optimization of area response of N,N-Bis(2-hydroxyethyl) dodecylamine depending on solvent extraction type in SALLE procedure. Acetonitrile on the left and isopropanol on the right analyzed by UHPLC–MS/MS.

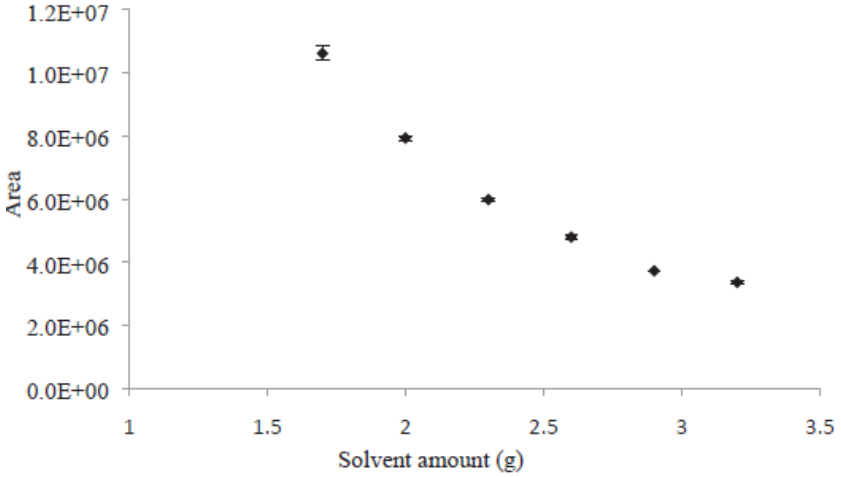

Fig. 1b. Optimization of area response of N,N-Bis(2-hydroxyethyl) dodecylamine depending on amount of ACN solvent extraction in SALLE procedure. Analyzed by UHPLC–MS/MS.

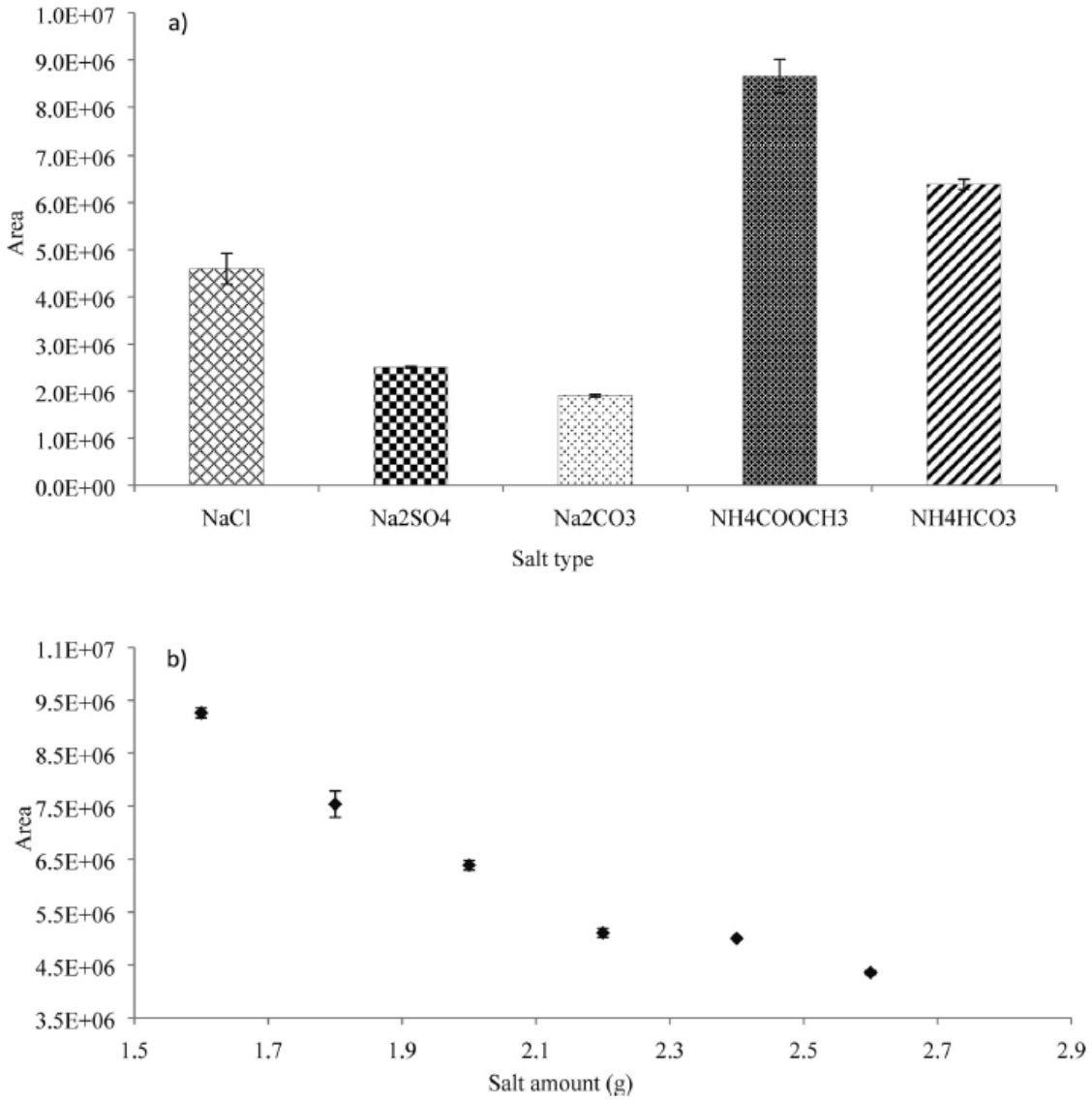

Fig. 2. The analytical signal of N,N-Bis(2-hydroxyethyl) dodecylamine analyzed by UHPLC–MS/MS against a) different salts added in SALLE procedure; b) amount of NH4COOCH3 added in SALLE procedure.

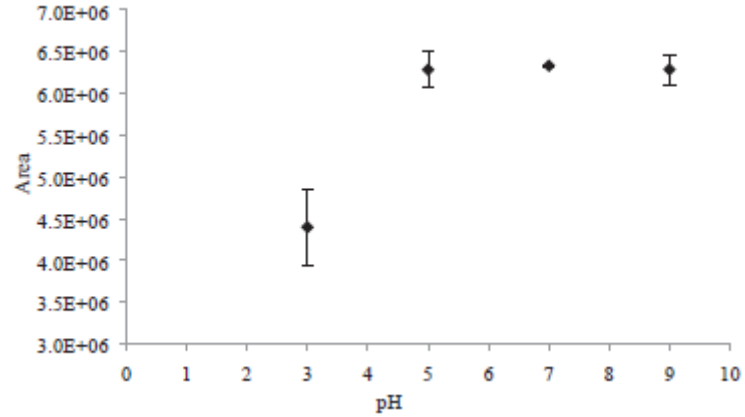

Fig. 3. Influence of pH on the area response of N,N-Bis(2-hydroxyethyl) dodecylamine extraction for SALLE procedure, analyzed by UHPLC–MS/MS.