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A 4-hydroxy-*N*′-[(*E*)-(2-hydroxyphenyl)methylidene]benzohydrazide-based sorbent material for the extraction-HPLC determination of biogenic amines in food samples

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ABSTRACT

A sorbent material based on a newly synthesized hydrazone ligand, 4-hydroxy-*N*′-[(*E*)-(2-hydroxyphenyl)methylidene]benzohydrazide was prepared by immobilizing the ligand into a silica sol–gel matrix. The capability of the sorbent material for the extraction of seven biogenic amines (BAs), i.e., tryptamine (TRY), *β*-phenylethylamine (PEA), putrescine (PUT), cadaverine (CAD), histamine (HIS), tyramine (TYR), and spermidine (SPD) was studied. Under the adopted conditions, the sorbent showed good selectivity towards PUT, CAD, HIS and SPD (% extraction (%E) > 96) while %E for TYR, TRY and PEA were 82.0, 78.9 and 46.4%, respectively. The sorbent could be used up to six extraction cycles for SPD, CAD and PUT and was applied to the determination of food samples ("budu", ketchup, orange juice, soy sauce) that were spiked with 20 mg L^{-1} of the BAs. The extracted analytes were derivatized with dansyl chloride before the HPLC determination. With the exception of HIS and TYR in "budu" sample, reasonable recoveries were found for the other analytes in all the tested food samples.

1. Introduction

Modern society place high expectations on the food industry to ensure high standards in producing, processing and supplying healthier food products as priority for healthy living. This in turn has put much pressure on the food manufacturers to adopt high quality control measures and ensure strict safety procedures before their products get into the market. One common problem is the production of the highly toxic metabolites known as biogenic amines (BAs). These compounds can seriously result in food intoxication with neurological and digestive symptoms in humans such as headache, palpations, diarrhea and vomiting [1,2].

BAs are produced in plants and animals by microbial decarboxylation of amino acids that resulted in the removal of α-carboxyl group to produce the corresponding amine. BAs can be of aliphatic, aromatic, (structures and pKa values are presented in our previous work [3]), and they are also of interest for their role as biomarkers in toxicological risk studies and as indicators of food quality [4]. The more important BAs in food are the diamines (e.g. putrescine (PUT) and cadaverine (CAD)), polyamines (spermidine (SPD) and spermine (SPM)), aromatic amines (e.g. tyramine (TYR)); and heterocyclic amines (e.g. tryptamine (TRY) and histamine (HIS)) [5]. BAs concentrations are normally lower in non-fermented food (e.g., fruits, vegetables, meat, milk and fish), but are higher in fermented foods (e.g., cheese, soybean products) and beverages as a result of a contaminating microflora exhibiting amino acid decarboxylase activity [4,6]. A considerable number of researchers had reported the occurrences of BAs in human tissues [7], plants [8], foods and food products such as fish and seafood [9], meat products [10], fruits and vegetables [11], and wine and alcoholic beverages [12].

Numerous analytical techniques have been reported for the determination of BAs in food products. Common sample extraction and clean up techniques used were liquid–liquid extraction (LLE) [13], solid phase extraction (SPE) [14], and liquid phase microextraction (LPME) [3]. These sample preparation methods are used in conjunction with analytical methods such as, capillary electrophoresis [15], high performance liquid chromatography (HPLC) [16,17], and gas chromatography [18]. Of these, SPE in conjunction with HPLC techniques enjoyed wide acceptance. The SPE techniques are mainly based on commercial sorbents such as C_{18} materials which are not suitable for polar analytes such as BAs. A selective SPE procedure using chemically modified polymer resin with crown ether was reported for the extraction of urinary catecholamines [19]. Recently, we have also reported a sorbent material based on the chemically immobilized crown ethers for the selective extraction of BAs [14]. However, this sorbent was found to be

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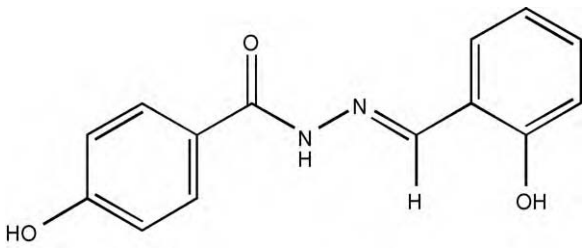

Fig. 1. Chemical structure of the synthesized hydrazone ligand, 4-hydroxy-*N*′-[(*E*)-(2-hydroxyphenyl)methylidene]benzohydrazide.

selective towards only one BA (SPD). Therefore, further studies are required to improve the selectivity towards the BAs.

In this paper, a new hydrazone ligand, 4-hydroxy-*N*′-[(*E*)-(2-hydroxyphenyl)methylidene]benzohydrazide, was synthesized (Fig. 1). The ligand was next physically immobilized within a silica sol–gel matrix and was used as sorbent in the selective extraction of BAs. The extracted BAs were desorbed, derivatized and analyzed using reversed-phase HPLC. As will be shown later; good selectivity was achieved towards PUT, CAD, HIS and SPD (% extraction (%E) > 96).

2. Experimental

2.1. Chemicals and reagents

Analytical grade chemicals, reagents and solvents were used as received without additional purification. Spermidine trihydrochloride, putrescine dihydrochloride, histamine dihydrochloride, β-phenylethylamine, tryptamine hydrochloride cadaverine, tetraethoxysilane (TEOS), ethanol, and tris(hydroxymethyl)aminomethane (Tris) were supplied from Sigma–Aldrich (Steinheim, Germany). Tyramine hydrochloride and dansyl chloride (5-dimethylaminonaphthalene-1-sulfonyl chloride) were supplied from Fluka (Buch, Switzerland). Acetonitrile and methanol (HPLC grade) were purchased from Fisher Scientific (Leicestershire, UK). Sodium hydroxide, glutamic acid monosodium monohydrate and hydrochloric acid were from Acros Organics, New Jersey, USA. Tetrahydrofuran (THF) was from Lab-Scan Asia (Bangkok, Thailand) while sodium hydrogen carbonate was purchased from BDH (Poole, England). 18 mΩ ultrapure water (Nanopure Diamond, Barnstead, USA) was used throughout.

2.2. Instrumentation

A Perkin Elmer 200-series HPLC unit consisting of pump, vacuum degasser, autosampler and diode array detector was used. An ultraviolet–visible lambda 35 UV–vis spectrometer was also used. Stuart Scientific flask shaker SFI (500 osc min^{-1}) was used for the extraction.

2.3. Chromatographic conditions

Chromatographic separation in the isocratic mode was carried out using a C_{18} ODS Hypersil column (250 × 4.5 mm, 5 μm) at ambient temperature. The mobile phase was 60:25:15 (v/v/v) acetonitrile:water:methanol at a flow rate of 1.0 mL min^{-1}; wavelength, 254 nm; injection volume, 50 μL. Unless otherwise stated, preparations and determinations were done in triplicates.

2.4. Preparation of sorbent

The hydrazone ligand was synthesized as was previously reported [20]. The sorbent was prepared by stirring a mixture of TEOS (3.28 mL), ethanol (4.56 mL), and HCl (0.36 mL, 4 M) for 15 min to yield a sol solution. Next, the hydrazone ligand (dissolved in 10 mL THF) was added to the sol solution and was stirred vigorously for 45 min. The solution mixture was clear and homogeneous, which was later aged in an oven (60 °C) for 2 days. The sol–gel that was formed was soaked in water for 1 day for conditioning. The sorbent was next dried (60 °C) for 1 day and ground into small pieces using a mortar and pestle. Blank sorbent was prepared by the same procedure except that no hydrazone ligand was added.

2.5. Leaching studies

Leaching of the hydrazone ligand from the sorbent material was studied according to the procedure as proposed by Yapa et al. [21]. The effects of exposure to organic solvents (ethanol, methanol and acetonitrile) and aqueous solutions (water, 0.1 M HCl and 0.1 M Tris buffer (pH 9)) were investigated. Sorbent material (25 mg) was shaken in each test solution (5 mL) for a maximum of 1440 min. After 30 min, it was filtered and the spectra of the filtrate were obtained using a UV–vis spectrophotometer. The UV–vis spectrum (200–800 nm) was obtained at 15 min interval till the end of the experiment (1440 min).

2.6. Preparation of standard solutions

Stock solution (1000 mg L^{-1}) of a mixture of seven BAs containing salts of TRY (61.4 mg), PEA (65.1 mg), PUT (91.5 mg), CAD (85.7 mg), HIS (82.8 mg), TYR (63.2 mg) and SPD (87.7 mg) was prepared in water. The solution was stored in the dark at 4 °C. The stock solution was diluted with water to yield the appropriate working solutions. To obtain the calibration curve, the working solution (1 mL) was derivatized and injected into the HPLC unit.

2.7. Derivatization procedure

The derivatization was carried out as previously reported [14]. In a sample vial, standard or sample extract (1 mL) was mixed with saturated $NaHCO_3$ (200 μL), 2 M NaOH (50 μL) and 2 mL of dansyl chloride (10 mg of dansyl chloride in 1 mL acetone, daily prepared). The mixture was heated (70 °C) on a water bath for 10 min. After the reaction was completed, glutamic acid (1 mL) was added to the reaction mixture in order to remove the unbound dansyl chloride and the solution was left to stand for 1 h at room temperature. The volume of the solution was then adjusted to 5 mL using acetonitrile.

2.8. Extraction of BAs

Batch method of extraction was conducted. The sorbent (25 mg) was placed in a glass vial along with 1 mL BAs standard mixture (100 mg L^{-1}) and 4 mL of 0.1 M Tris buffer (pH 9) to adjust the pH of the solution. The mixture was shaken mechanically at room temperature (25 °C) for 15 min. After the equilibrium time, the mixture was filtered and the filtrate (1 mL) was derivatized. The amount of the un-extracted BAs left in the solution after the extraction was determined by reversed-phase HPLC.

Once the extraction was completed, the BAs were desorbed by shaking the sorbent with 0.1 M HCl (5 mL) for 30 min, the solution was filtered and the filtrate (1 mL) was derivatized. The amount of the stripped BAs was determined by reversed-phase HPLC. The sorbent was rinsed several times with water and dried (60 °C) before the next extraction cycle was conducted. The extraction and stripping cycle were repeated six times.

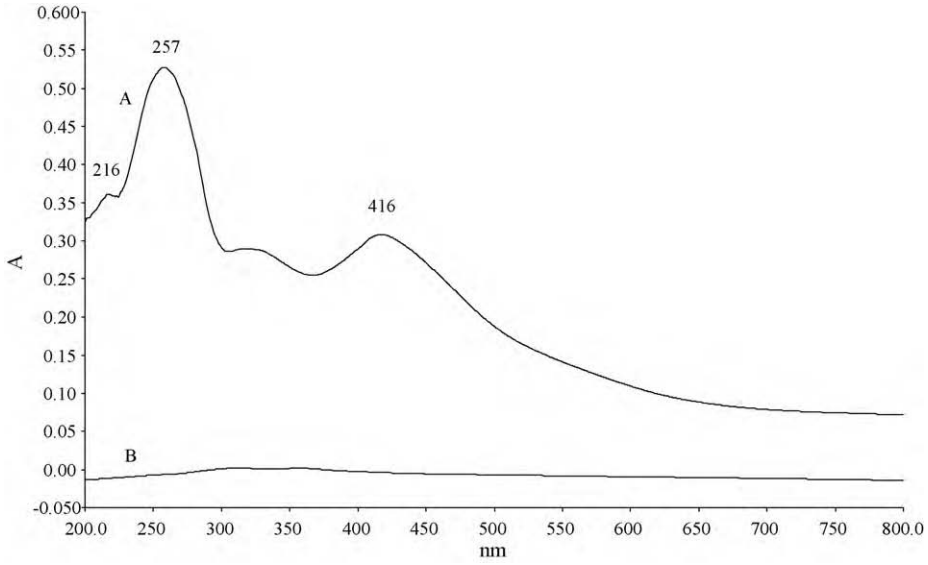

Fig. 2. Solid state UV–vis spectra of (A) blank, and (B) hydrazone immobilized sorbents.

2.9. Determination of BAs in food samples

Food samples (tomato ketchup, soybean sauce, orange juice and a local fish sauce "budu") were purchased from local markets in Penang, Malaysia. Each food sample (5 g) was accurately weighed and extracted twice with 0.1 M HCl (10 mL) and homogenized for 5 min. The homogenates were centrifuged (4000 rpm) for 15 min at 4 °C. The supernatant was filtered using a Whatman 42 filter paper, spiked with 1000 mg L^{-1} (1 mL) standard BAs. The pH was adjusted to 9 using 0.1 M Tris buffer and top – up to the 50 mL mark with water. 5 mL of the sample was shaken together with the sorbent (25 mg) for 15 min at room temperature. The sample was then filtered and the extracted BAs were desorbed by shaking the sorbent with 0.1 M HCl (5 mL) for 30 min. This solution (1 mL) was derivatized and injected into the HPLC unit.

3. Results and discussion

3.1. Characterization of sorbents

Initially, FTIR was used to provide evidence of the presence of the hydrazone ligand in the sol–gel matrix. However, it was found that both the blank and the ligand immobilized sorbents produce identical spectra. This could be attributed to the small amount of the hydrazone in the silica network, as was also experienced by other researchers [22,23]. The UV–vis spectra of the blank and the hydrazone immobilized sorbents are shown in Fig. 2. The immobilized hydrazone ligand displayed maximum absorption peak λ_{max} at 216 nm that was assigned to C=O in the amide group. Another absorption peak at 257 nm was assigned to C=N. The absorption peak in the visible region were observed at 416 nm due to C=NNH group. Accordingly this strong evidence indicates the successful incorporation of the hydrazone ligand into the sol–gel network [24].

3.2. Analytical characteristics of the HPLC method

An earlier HPLC method for the separation of BAs used 65:35% acetonitrile (ACN):water as mobile phase [14]. The components were separated in about 27 min. In an attempt to further reduce the run time, variation of methanol (0–20%), water (20–40%), ACN (50–70%) and flow rate (0.8–1.4 mL min^{-1}) on the separation of the BAs were studied. The chromatographic conditions used were 60:25:15 (v/v/v) ACN:water:methanol at a flow rate of 1.0 mL min^{-1}. Under these conditions, all the studied dansylated amines were eluted in about 18 min.

Standards (0.001–50 mg L^{-1}) were prepared and found to be linear over this range for all the BAs. Results are summarized in Table 1. The linearity of the calibration curves was studied by injecting seven concentrations of standard mixtures. All the analytes showed good linearity with squared regression coefficient (r^2) ranging from 0.9999 to 1.0000. The limits of detection (LOD) and quantification (LOQ) based on signal-to-noise ratio (S/N) of 3 and 10, were in the range of 0.02–0.06 μg L^{-1} and 0.07–0.19 μg L^{-1}, respectively. These values are lower than those reported in the literature (LOD 0.47–16.80 μg L^{-1}) [25], and (LOD (6–217) and LOQ (19–724) μg L^{-1}) [26]. The large sample volume (50 μL) injected is partly responsible for the improvements in the LOD and LOQ.

Table 1
Analytical characteristics of the HPLC method.

BA	Linear range (mg L^{-1})	Regression equation	r^2	LOD (μg L^{-1})	LOQ (μg L^{-1})	Intra-day (% RSD) (n = 9)	
						t_R	Area
TRY	0.001–50	$y = 167666x$	1.0000	0.04	0.13	0.77	2.10
PEA	0.001–50	$y = 117628x$	1.0000	0.06	0.19	0.86	1.07
PUT	0.001–50	$y = 242371x$	0.9999	0.03	0.09	0.97	1.43
CAD	0.001–50	$y = 241921x$	1.0000	0.03	0.09	1.06	1.86
HIS	0.001–50	$y = 262089x$	1.0000	0.03	0.09	0.74	2.08
TYR	0.001–50	$y = 259471x$	1.0000	0.03	0.09	1.33	0.98
SPD	0.001–50	$y = 304284x$	1.0000	0.02	0.07	0.52	1.05

BA = biogenic amine.

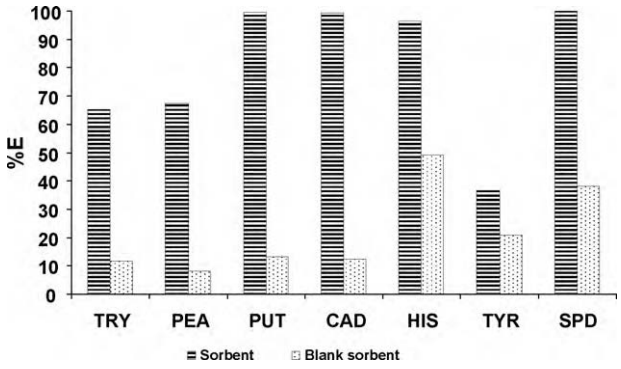

Fig. 3. Extraction of biogenic amines using blank and hydrazone immobilized sorbent. Extraction conditions: 25 mg sorbent; extraction time, 15 min; BAs concentration, 20 mg L^{-1}.

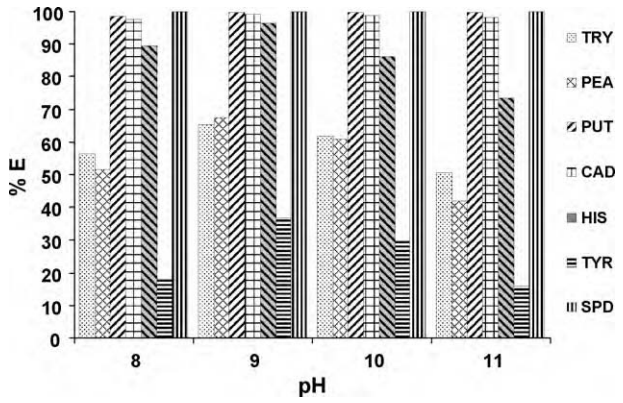

Fig. 4. Effect of sample pH on the extraction of biogenic amines. Extraction conditions: 25 mg sorbent; extraction time, 15 min; BAs concentration, 20 mg L^{-1}.

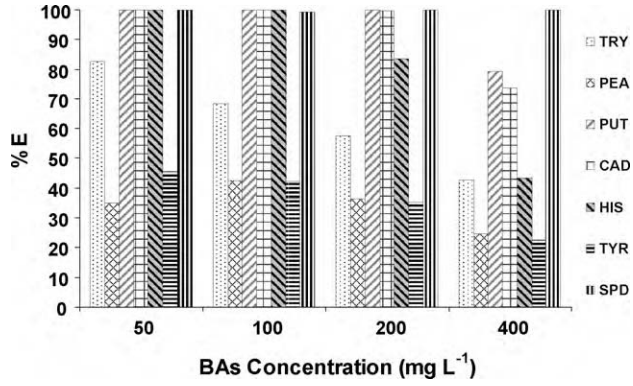

Fig. 5. Effect of biogenic amine concentration on the extraction. Extraction conditions: 25 mg sorbent; extraction time, 15 min; pH 9.

The repeatability and reproducibility was investigated by injecting three different BAs mixtures thrice on the same day (intra-day). Good reproducibility of both peak areas (RSD = 2.10%) and retention times (RSD = 1.33%) were found.

3.3. Optimized parameters of extraction

The extraction was optimized by using 20 mg L^{-1} BAs standard solution. Important parameters that affects the extraction efficiency were investigated, i.e., sample pH, ligand concentration within the sorbent material, extraction time, and sorbent capacity.

The extraction was also carried out using blank sorbent (i.e. does not contain the hydrazone ligand) as control. The enhancement on the extraction behaviour between the blank and the ligand immobilized sorbents demonstrated the capability of hydrazone ligand in the extraction process (Fig. 3).

3.3.1. The effect of pH

The effect of sample pH (3–11) on the extraction efficiency was studied. At pH 3–6 no significant extraction was observed (data not shown) due to the protonation of the (N–H) amide group which minimized the delocalization resonance [27]. Moreover, repulsion will take place between the protic BAs and protic (N–H) at the amide group. The pH range for the quantitative extraction of BAs was found to be from 8 to 11. Within this pH range, deprotonation occurs at the (N–H) amide group [27] which maximizes the delocalization resonance and provides extra charge/charge interaction between the protic BAs and the amide group. The optimum pH for the extraction of the studied BAs was pH 9. Over pH 9, the amino group of TRY, PEA, HIS, and TYR is unprotonated while at pH 8 there is insignificant deprotonation of the (N–H) amide group. At pH 9, good extraction of SPD (100%E), CAD (99.2%E), PUT (99.6%E) and HIS (96.5%E) was observed (Fig. 4).

3.3.2. Effect of contact time

The effect of contact time on the extraction efficiency was studied by shaking the BAs mixture with the sorbent ranging from 5 to 60 min at pH 9. Good extraction was observed after 5 min of contact time (%E > 79%) for all the studied BAs (results not shown). However, maximum extraction was achieved after 15 min; increasing the contact time further has no significant improvement of the %E. Therefore, 15 min contact time was chosen for subsequent studies.

Table 3
Capacity of the sorbent (mmol g^{-1}) with different concentrations of BAs.

BA	BA (mg L^{-1})			
	50	100	200	400
PUT	0.023	0.045	0.091	0.140
CAD	0.011	0.023	0.046	0.067
HIS	0.018	0.036	0.060	0.062
SPD	0.014	0.028	0.055	0.100

Table 2
Reusability of sorbent through six extraction cycles ($n = 2$).

BA	% Extraction					
	1	2	3	4	5	6
TRY	78.7	73.1	68.4	67.6	65.7	63.7
PEA	46.4	40.9	31.1	29.2	28.4	26.2
PUT	99.2	99.2	99.0	94.1	89.5	84.8
CAD	98.1	96.5	95.7	92.5	87.1	81.5
HIS	96.2	80.1	52.9	50.9	40.9	32.8
TYR	82.0	79.6	63.5	58.4	56.3	51.4
SPD	100.0	100.0	92.6	100.0	100.0	100.0

Extraction conditions: 25 mg sorbent; extraction time, 15 min; pH 9; ligand concentration, 0.85%; BAs concentration, 20 mg L^{-1}.

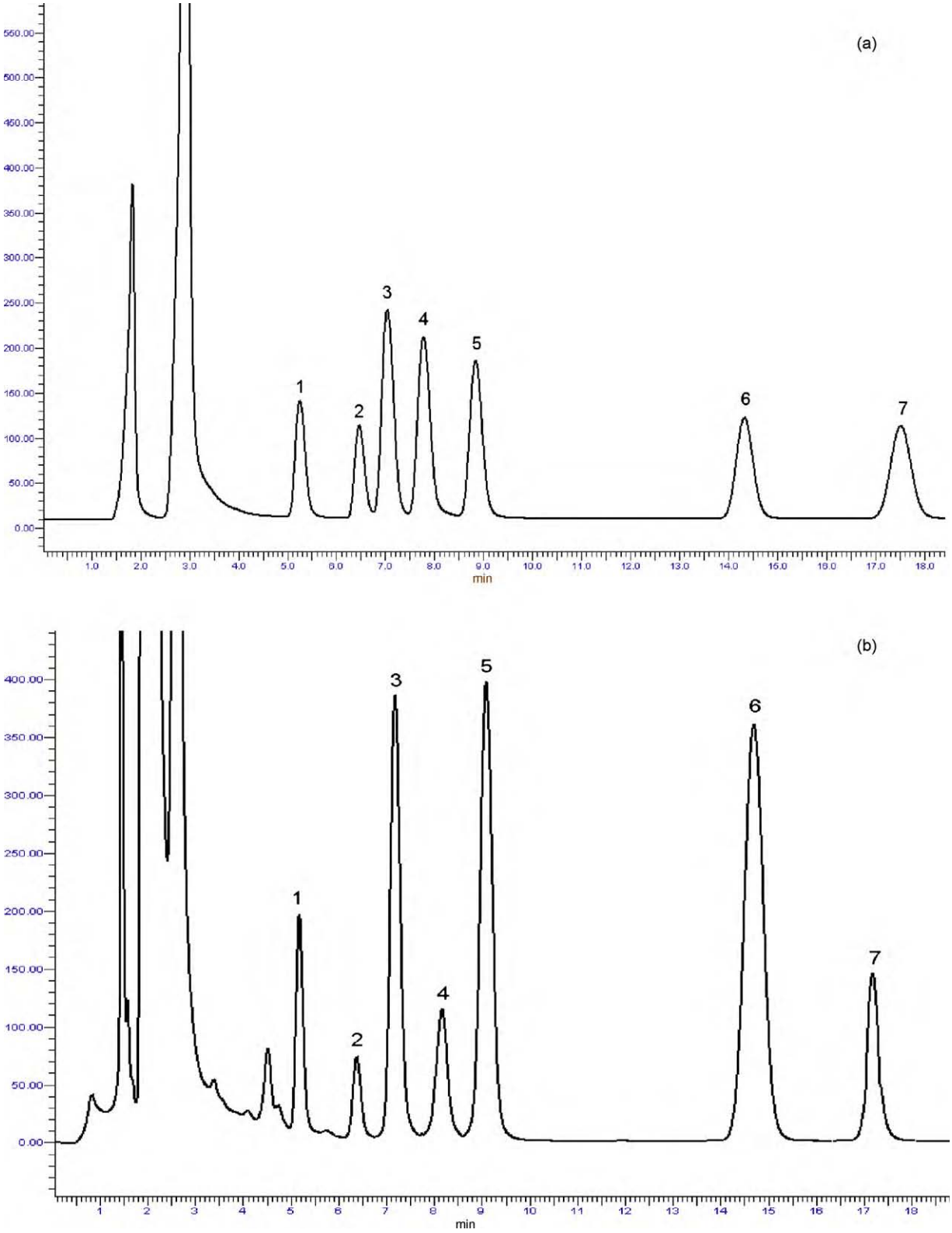

Fig. 6. Chromatograms of (a) BAs (20 mg L^{-1} each) standard solution, (b) "budu" extract spiked with 20 mg L^{-1} BAs after clean up with hydrazone-based sorbent. Peak identification: TRY (1); PEA (2); PUT (3); CAD (4); HIS (5); TYR (6); SPD (7).

3.3.3. Effect of ligand concentration in the sol–gel network

Sorbent materials containing different concentrations of ligand (0.85–6.8%) were prepared and their extraction efficiency was examined at the optimum pH 9 and extraction time of 15 min. It was observed that the highest extraction (%E > 80) for all BAs was obtained when 0.85% ligand in the sorbent was used. Further increase of the ligand concentration does not seem to affect the extraction efficiency.

Table 4
Concentrations of biogenic amines found in food samples.

Food sample	BA ($\mu g\,g^{-1}$)						
	TRY	PEA	PUT	CAD	HIS	TYR	SPD
Budu	304.0	231.0	159.0	237.5	367.5	619.5	157.0
Ketchup	67.0	119.5	108.5	91.5	63.5	88.5	78.0
Orange juice	67.5	62.5	113.5	99.0	50.0	89.0	76.0
Soybean sauce	55.0	121.0	108.0	85.0	85.0	80.5	63.5

Table 5
Recoveries (%) of BAs from spiked food samples[a].

Food samples	BA						
	TRY	PEA	PUT	CAD	HIS	TYR	SPD
Budu	57.1 ± 4.5	97.6 ± 4.1	100.0 ± 0.5	74.8 ± 1.1	8.5 ± 5.6	8.6 ± 5.2	98.9 ± 0.6
Ketchup	75.2 ± 2.1	91.6 ± 2.6	99.5 ± 0.6	99.7 ± 0.8	73.3 ± 3.3	74.3 ± 1.6	97.5 ± 2.4
Orange juice	79.0 ± 3.2	91.1 ± 1.4	97.3 ± 2.1	98.4 ± 0.4	67.3 ± 4.1	68.8 ± 3.6	96.0 ± 0.8
Soy sauce	72.5 ± 1.5	92.1 ± 2.2	98.4 ± 1.6	97.6 ± 1.3	69.1 ± 2.3	71.2 ± 3.8	97.1 ± 3.2

[a] Level spiked, 20 mg L^{-1}.

3.3.4. Leaching studies

Significant loss of the hydrazone ligand, due to its leaching from the sol–gel network when the sorbent is exposed to organic solvents (ethanol, methanol, acetonitrile) was observed. However in aqueous solutions (H_2O, HCl and Tris buffer) no noticeable loss of the ligand was observed over the period tested (data not shown). Therefore, these organic solvents were avoided in the desorption step.

3.3.5. Reusability

The performance of the sorbent material under repeated use was tested by performing the extraction–desorption through six extraction cycles. The stripping reagent used for desorption was 0.1 M HCl (5 mL). With the exception of HIS, PEA and TYR, the sorbent still maintained its extraction ability through six extraction cycles (Table 2). The extraction of the aliphatic BAs was satisfactory under these conditions.

3.3.6. Capacity of sorbent

Four different concentrations (50–400 mg L^{-1}) of BAs were used to study the extraction efficiency and the capacity of the sorbent (Fig. 5). It was found that the aliphatic BAs (PUT, CAD, and SPD) were quantitatively extracted (%E 100%) up to 200 mg L^{-1}. At concentrations higher than 200 mg L^{-1} a decrease in the extraction of PUT and CAD was observed, while no decrease was found for SPD. The aromatic BAs were also poorly extracted than the aliphatics. The presence of the aromatic ring resulted in a decrease in the extraction efficiency due to steric effects. HIS was extracted more than the other aromatic BAs due to its smaller size.

The capacity of a sorbent is defined as the mmol of analyte extracted/g of sorbent. The capacity was found to be dependent on the initial concentration of PUT, CAD, HIS and SPD in the solution (Table 3). As the concentration of PUT, CAD, HIS and SPD increase, the capacity value of the sorbent also increases. The highest value of the capacity was found for PUT (0.023–0.190 mmol g^{-1}). The capacity of this sorbent is slightly inferior to the sorbents based on silica gel immobilized aliphatic amines and imprinted organic–inorganic hybrid (e.g., 0.1–3.1 mmol g^{-1}) [28,29] but higher than the sorbents based on the immobilized thia crown ethers ($1.6–33.4 \times 10^{-3}$ and $3.8–85.9 \times 10^{-5}$ mmol g^{-1}) [14,22].

3.4. Adopted extraction conditions

The adopted extraction conditions were: sorbent mass, 25 mg; tris(hydroxymethyl)aminomethane buffer (0.1 M), pH 9; contact time, 15 min; ligand concentration, 0.85%.

3.5. Extraction of BAs from real samples

In order to investigate the viability of the studied sorbent, four samples, namely a local fish sauce ("budu"), ketchup, orange juice and soy sauce were used. The concentrations of the BAs found in the samples when analyzed using a previously reported method [30] are shown in Table 4. Relatively low levels of BAs were found in most of the studied samples. The results of the recoveries are shown in Table 5, while representative chromatograms of the standard and the real samples are showed in Fig. 6. Satisfactory recoveries were obtained for all BAs in orange juice (67.3–98.4%), ketchup (73.3–99.7%), and soy sauce (69.1–98.4%), while "budu" sample showed good recoveries for PEA, PUT, CAD, and SPD only. The lower recoveries obtained for HIS and TYR were due to their higher content in the "budu" sample (Table 4), which exceeds the capacity of the sorbents. "Budu" samples were chosen for the studies as the fish/shrimp fermented samples represent complex matrix.

4. Conclusion

A new sorbent material based on the physical immobilization of a synthesized hydrazone ligand within a silica sol–gel matrix was prepared. The sorbent shows preferential selectivity towards the aliphatic (PUT, CAD, SPD) and the heterocyclic (HIS) over the aromatic (TRY, PEA, TYR) BAs and was applied for the extraction of BAs in different food samples. With the exception of "budu" samples, reasonable recoveries were found in ketchup, soy sauce and juice. A significant advantage of the hydrazone ligand when compared with sorbents based on crown ethers is that the hydrazone can be easily synthesized using a simple step at room temperature [31]. Furthermore, the starting materials (phenylehydrazines and ketone or aldehyde compounds) are cheaper than their crown ether counterparts [32].

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