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Electrolytically produced copper(I) chloride on the copper wire as an excellent sorbent for some amines

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Abstract

A new solid-phase microextraction (SPME) fiber has been developed and applied for the determination of some amines (*n*-pentylamine, tripropylamine, dibutylamine, diisobutylamine and tributylamine). In this study two copper wires were immersed in sodium chloride solution and electrolysis was performed at a constant potential. Anode was oxidized to copper(I) to produce copper(I) chloride as a sorbent for the studied amines on the copper wire. Several parameters affecting the fiber preparation and SPME procedure such as electrolysis time, selection of the SPME coating, extraction time and temperature were optimized. The copper(I) chloride fiber was the most appropriate one for the determination of amines by SPME–GC–FID. The optimized method was linear over the range studied (1–100 $\mu g\ L^{-1}$) and showed good precision, with R.S.D values less than 3% for all analytes. Fiber production was reproducible and R.S.D for fiber-to-fiber was less than 8%. The proposed SPME–GC method showed some advantages such as lower detection limits, a shorter analysis time and the avoidance of expensive commercial fibers.

Keywords: Gas chromatography; Solid-phase microextraction; Copper(I) chloride fiber; Gaseous samples; Lower amines

1. Introduction

Sample pre-treatment and preconcentration is generally required for the determination of trace organic pollutants. Solid-phase microextraction is an alternative to solid-phase extraction and liquid–liquid extraction is simple, sensitive, time-efficient and solvent-free [1]. The analytes are extracted onto the fibers from the liquid phase or the headspace above the sample, and then thermally desorbed in the injector of the gas chromatograph. In order to achieve higher selectivities for different kinds of compounds, various materials such as polydimethylsiloxane [2–5], polyacrylate [6–8], carbowax–divinylbenzene [9,10], polyimide [11], carbopack [12] and polypyrrole [13] have been used as the stationary phases of the fibers. However, all these stationary phases are normally deposited physically on the surface of the fused-silica rods, which may be responsible for the lower thermal and chemical stability of the fiber. Fibers based on metallic wires overcome to these problems. Recently, activated charcoal in PVC matrix was used to adsorb *n*-alkanes [14,15] and organophousphorous pesticides [16] and cellulose acetate in the same matrix for adsorption of alkanes [17]. The former sorbents were coated on silver or copper wires. Durability of these fibers was excellent thermally, chemically and mechanically.

Amines are widely used in industry for making dyes, cosmetics and medicines, and as intermediates in many chemical syntheses [18,19]. Many amines are proven or suspected to be carcinogenic and have been implicated in inducing cancer of the bladder [20,21]. Therefore, the monitoring of their levels in environmental samples is important for the protection of health and the environment. These compounds have been included in the US Environmental Protection Agency (EPA) list of priority pollutants [22,23].

In the present study, three copper compounds were coated on the copper wire using electrolysis at a constant potential. Efficiency of the obtained fibers was

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investigated by the extraction of amines from the gaseous samples.

2. Experimental

2.1. Chemicals and reagents

The following amines were studied: *n*-pentylamine, tripropylamine, dibutylamine, diisobutylamine and tributylamine. These compounds with purity above 99% were supplied by E. Merck (Darmstadt, Germany). Sodium chloride, sodium sulfide and sodium hydroxide (all analytical-reagent grade; Merck) were used as electrolyte in the preparation of fiber. Methanol (analytical-reagent grade; Merck) was used as solvent for amines.

A standard solution was prepared by transferring 10 μL of each compounds in a volumetric flask and diluting with methanol to 10 mL at room temperature and stored at 4 °C.

2.2. SPME fiber preparation

The fibers used in this study were copper wire coated with different copper(I) compounds (chloride, oxide and sulfide). These coatings were produced by electroplating at a constant potential (12 V and 300 mA). It is mentioned that other potentials were also examined in the fiber preparation. At lower potentials the production of fiber was disturbed (less than 2 V) or longer time was consumed in its production. On the other hand, electroplating at higher voltages (higher than 15 V) produced fiber, which was unstable mechanically. It did not adhered on the support (copper wire). Electrolyte was 0.1 M sodium chloride, sodium hydroxide or sodium sulfide. Both electrodes, copper wires, were immersed in the electrolyte and electrolysis was performed for 5 min. During the electrolysis process the insoluble copper compounds were produced on the anode. The produced sorbents were conditioned before use, by inserting them into the GC injector for 15 min at 300 °C.

2.3. Chromatography

The analyses were carried out on an STG GC-101b gas chromatograph (Sanayeh Teif Gostar, Tehran, Iran) equipped with a split/splitless injector and a flame ionization detection (FID) system. The injection was made in the splitless mode for 5 min. The chromatographic conditions were optimized and finally the following conditions were selected: injection temperature, 300 °C; column, OPTIMA-5-Amin capillary column (30 m × 0.25 mm i.d., 0.50 μm film thickness) (Macherey-Nagel); oven temperature programme, 35 °C (5 min), 7 °C min^{-1}, 130 °C (10 min) and detector temperature, 250 °C. The carrier gas was nitrogen with a column-head pressure of 20 psi (1 psi = 56894.76 Pa). The FID detector was fed with 30 mL min^{-1} of hydrogen, 300 mL min^{-1} of air and 30 mL min^{-1} of nitrogen as make-up gas.

2.4. Solid-phase microextraction procedure

To prevent the polar analytes from being extracted onto the glass wall, the extraction vessel (100 mL volumetric flask) were acid washed and silanized prior to the experiments. To prepare the gaseous samples for optimization of the extraction process, 2 μL of the standard solution was injected to an extraction vessel. The resulted sample had the following concentrations: pentylamine, 15.0 μg L^{-1}; tripropylamine, 15.0 μg L^{-1}; dibutylamine, 15.2 μg L^{-1}; diisobutylamine, 14.9 μg L^{-1} and tributylamine 16.0 μg L^{-1}. The fiber was exposed to the analytes in gaseous phase for 15 min at 10 °C and then transferred to the injector to be desorbed (300 °C, 5 min). Cleaning of the extraction vessel was carried out before the next experiment. It was hold in an oven at 150 °C for 5 min and then nitrogen was purged for 10 min. All studies were made in triplicate and average values were calculated.

3. Results and discussion

3.1. Optimization of desorption conditions

The optimization of thermal desorption has an important influence on precision, sensitivity, retention time and peak shape. We tested desorption times (1, 2, 3, 5, 7.5 and 10 min) and temperatures (100, 150, 200, 250, 300 and 350 °C) for all analytes in the injector. Desorption of the analytes was completed using the splitless mode at 300 °C as injector temperature and 5 min as desorption time.

3.2. Selection of fiber

To select the best fiber, three fibers (chloride, oxide and sulfide) were constructed in the similar conditions with the exception of electrolyte type. They were exposed to the gaseous samples containing target amines. It was observed that the copper(I) chloride fiber extracted all amines, more than others (with the except tripropylamine). The adsorbed analytes by the oxide and sulfide fibers (normalized data relative to those obtained by the chloride fiber) are summarized in Table 1. Sulfide fiber did not extract pentylamine, whereas it extracted tripropylamine more than the chloride fiber. Chloride fiber showed the highest peak areas for other compounds. Therefore, this fiber was selected for optimization. In order to optimize the adsorption of amines by the chloride fiber the factors that influence the extraction equilibria (extraction time and vessel volume or sample size) were considered.

3.3. Influence of extraction time

The influence of the extraction time (0–30 min) for each compound using the chloride fiber was evaluated. The study was performed in the 100 mL volumetric flask, using 2 μL standard solution injected to it. After 15 min the increase in peak areas changed very little for most of the compounds, reaching the highest extraction between 15 and 30 min.

Table 1
Study of fiber type on the extraction of amines from gaseous phase

Fiber	Normalized peak areas				
	Pentylamine	Tripropylamine	Dibutylamine	Diisobutylamine	Tributylamine
Chloride	1.00	1.00	1.00	1.00	1.00
Oxide	0.08	0.03	0.38	0.13	0.44
Sulfide	0.00	1.37	0.60	0.23	0.80

3.4. *Influence of extraction temperature*

Fig. 1 represents the extraction temperature profiles for the amines in the mixture. It is shown that the extraction ability of the fiber increased with temperature at 10 °C, but decreased significantly at temperatures higher and lower than 10 °C. Extraction ability is mainly controlled by two factors, distribution velocity and partition coefficient. The distribution velocity, which helps analytes to move near the solid-phase coating, increases with increased temperature. Extraction is an exothermic process and the partition coefficient, which determines the ratio of analytes extracted, is inversely related to temperature. The first factor is dominant in the temperature range less than 10 °C, while the second becomes dominant at temperatures higher than 10 °C.

3.5. *Influence of sample size*

For this purpose 100 and 1000 mL vessels were selected and 2 μL of amines standard solution was transferred to them. Then the fiber was exposed to analytes in gaseous phase for 15 min at 10 °C. The peak areas obtained by injection of adsorbed amines on the fiber into GC were compared with those obtained from the direct injection of standard solution (Table 2). Extraction recoveries were higher than 50% for all analytes with the exception for dibutylamine when 100 mL sample was used. Pentylamine was completely extracted and two others (tripropylamine and diisobutylamine) were quantitatively adsorbed by the sorbent from 100 mL sample. Increasing sample size from 100 to 1000 mL decreased recovery of analytes to 2–32%. However in the following studies 100 mL was used as sample volume to obtain a high sensitive method for analysis of amines.

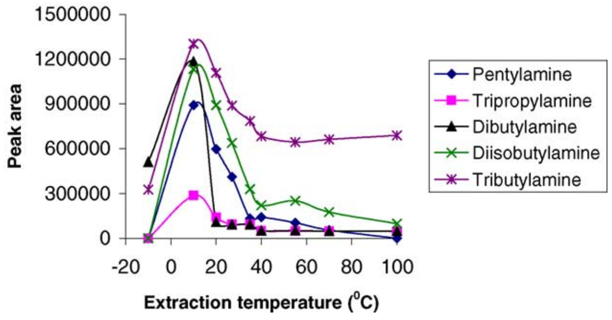

Fig. 1. Influence of extraction temperature on the signal intensity of amines. Extraction time, 15 min; desorption time, 5 min.

3.6. *Selection of sample type (gaseous versus solution)*

Although gaseous samples have some advantages, such as avoiding from contamination of fiber, increasing its lifetime and rapid extraction, a comparative study between gaseous and solution samples of amines was carried out in order to establish the efficiency of the fiber. In the case of solution, fiber was placed in the headspace of sample. The extraction was carried out at pH 7 and 12. The results obtained for both solutions along with extraction from gaseous sample using the same amount of analytes and for 15 min as extraction time are presented in Fig. 2. As can be seen all extracted compounds showed greater peak areas in the extraction from gaseous sample in comparison with those obtained from the solution samples with the exception of pentylamine in solution with pH = 12 and thus the gaseous sample was selected for further studies. This behavior can be explained because there is a relatively high concentration of hydroxide ions in pH = 12, which facilitate transition of relatively volatile amine, pentylamine to gas phase. This also shows that in spite of deactivation of extraction vessel there are some unreacted silanol groups, which adsorb amines compounds. On the other hand, water vapor competes with amines in adsorption onto the active sites of the fiber. Therefore, adsorption efficiency of fiber decreased in the case of solution sample as compared with gaseous sample for most analytes.

3.7. *Complete removal of amines by the proposed fiber*

To remove amines from the gaseous sample, the successive extractions were carried out on a single sample and the

Table 2
Study of sample size on the extraction of amines from gaseous phase and its comparison with direct injection

Analyte	Direct injection	Sample size	
		100 mL	1000 mL
Pentylamine	7.20×10^4 (100)	7.23×10^4 (100)	0.23×10^4 (3.2)
Tripropylamine	46.1×10^4 (100)	41.0×10^4 (89)	7.79×10^4 (17)
Dibutylamine	58.3×10^4 (100)	27.4×10^4 (47)	18.8×10^4 (32)
Diisobutylamine	102×10^4 (100)	95.3×10^4 (93)	2.16×10^4 (2)
Tributylamine	219×10^4 (100)	114×10^4 (52)	24.6×10^4 (11)

Data are peak areas (data in parentheses are normalized peak areas).

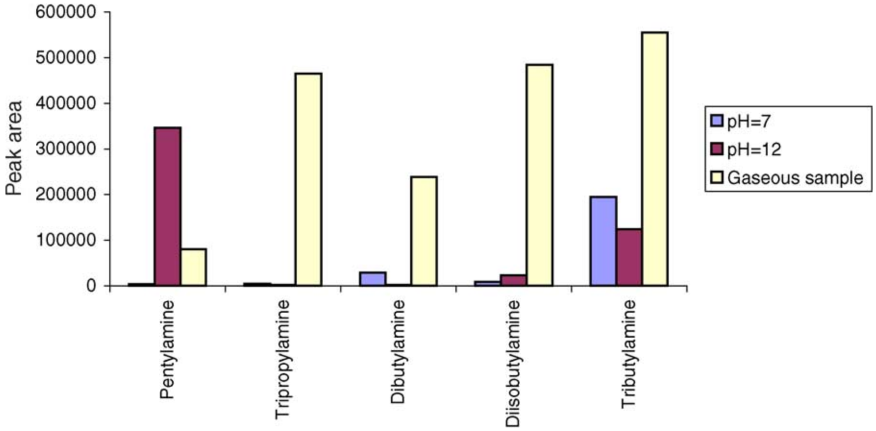

Fig. 2. Comparison of fiber efficiency in adsorption of amines from gaseous sample and headspace of solution sample.

extracted analytes rapidly injected into gas chromatograph. As can be seen from Fig. 3 pentylamine was completely extracted in the first extraction. Two others (tripropylamine and diisobutylamine) were also adsorbed higher than 90% in the first extraction. In general all studied compounds were quantitatively removed from the sample after six repeated extractions. These data show that the proposed fiber has high capacity relative to amines and the total exhaustion of some analytes is performed in the first extraction.

3.8. Influence of storage time on the amines adsorbed on the fiber

To evaluate the stability of amines adsorbed on the proposed fiber two experiments were carried out. After extraction fiber was retracted into the needle of SPME device and was hold for 12 h at room temperature. In another experiment after extraction fiber was hold in refrigeration at 4 °C for 10 h. Then the remained amines on the fiber were desorbed into the injection port of GC and quantification was performed on the resolved compounds. The peak areas obtained in both cases were compared with those obtained from the case in which adsorbed amines were introduced to the separation system immediately after extraction. The peak areas for all compounds changed during the storage period with exception of tripropylamine. This proposes that the extracted amines must be injected into gas chromatograph immediately after extraction.

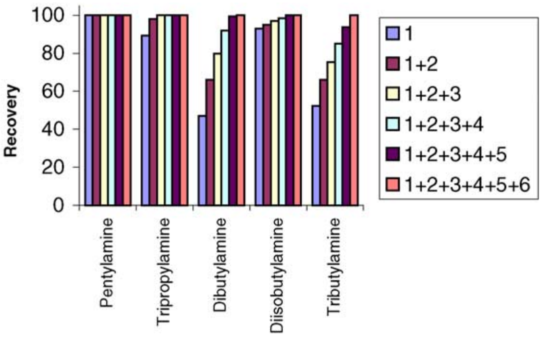

Fig. 3. Complete exhaustion of amines from gas phase by the successive extractions performed on a single sample. Cumulative recoveries were used in vertical axis.

3.9. Study of repeatability and reproducibility

In order to assess the repeatability (for one fiber) and the reproducibility, (fiber-to-fiber) three fibers were constructed under the same experimental conditions and six repeated experiments were carried out by each fiber. The relative standard deviations (R.S.D%) for each fiber and fiber-to-fiber were calculated and summarized in Table 3. These data show that repeatability of the method is excellent and R.S.D% for one fiber is less than 3% and for fiber-to-fiber 8%.

3.10. Performance evaluation of the proposed method

Linearity and detection limits were evaluated in order to access the performance of the proposed method. Results are shown in Table 4. The calibration studies were performed with chloride fiber using 100 mL spiked gaseous samples. These samples were analysed in duplicate at the optimal extraction conditions established by the design and the complementary experiments discussed above. Calibration curves were linear in the concentration range studied: from 2–50 μg L^{-1} for pentylamine and diisobutylamine, from 1–100 μg L^{-1} for tripropylamine and tributylamine, and from 1–70 μg L^{-1} for dibutylamine. As can be seen in

Table 3
The relative standard deviation for one fiber ($n = 6$) and fiber-to-fiber ($n = 3$)

Analyte	Relative standard deviation (R.S.D%)			
	Fiber 1	Fiber 2	Fiber 3	Fiber-to-fiber
Pentylamine	0.12	1.2	1.54	6.4
Tripropylamine	0.85	0.14	2.07	5.8
Dibutylamine	1.10	1.50	2.81	4.3
Diisobutylamine	0.17	0.34	0.34	8.1
Tributylamine	0.70	0.71	0.50	5.2

Table 4
Quantitative characteristics of the proposed method

Compound	Calibration curve equation	r[a]	LOD[b] ($\mu g\,L^{-1}$)	LDR[c] ($\mu g\,L^{-1}$)
Pentylamine	$A = 47173C-11550$[d]	0.998	0.7	2–50
Tripropylamine	$A = 320627C-79641$	0.998	0.35	1–100
Dibutylamine	$A = 88478C-5308.9$	0.997	0.35	1–70
Diisobutylamine	$A = 662512C-258386$	0.997	0.7	2–50
Tributylamine	A = 533555C−59700	0.999	0.35	1–100

[a] Correlation coefficient.
[b] Limit of detection.
[c] Linear dynamic range.
[d] A and C are peak area and concentration ($\mu g\,L^{-1}$), respectively.

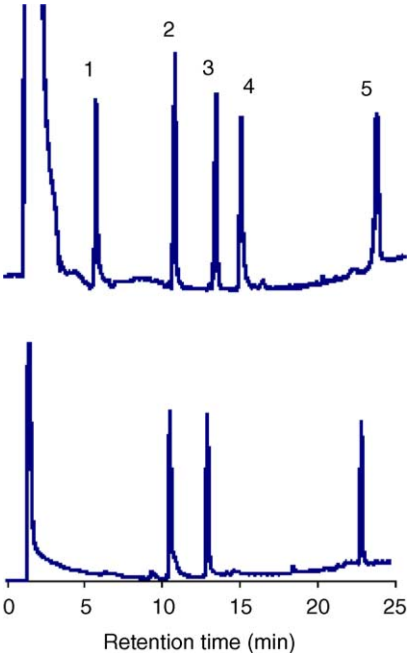

Fig. 4. Chromatographic separation of amines compounds adsorbed on the copper(I) chloride fiber from (a) standard sample, (b) laboratory atmosphere during an overnight; (1) *n*-pentylamine; (2) tripropylamine; (3) dibutylamine; (4) diisobutylamine and (5) tributylamine. For chromatographic conditions see the text.

Table 4 the correlation coefficients (r) values were higher than 0.997 for all of the compounds, so a directly proportional relationship between the extracted amount of amines and their initial concentrations in the samples at the tested concentration ranges is demonstrated. Detection limits (based on a signal-to-noise ratio 3) are shown in Table 4. These are 0.35 $\mu g\,L^{-1}$ for tripropylamine, dibutylamine and tributylamine and 0.70 $\mu g\,L^{-1}$ for pentylamine and diisobutylamine. To evaluate efficiency of the fiber in the real samples, it was exposed to the laboratory atmosphere for an overnight. Three amines were detected in the related chromatogram (Fig. 4).

4. Conclusions

A method for the preparation of fiber to sampling amines from gas phase has been optimized. Three different fibers were tested and the copper(I) chloride fiber showed good efficiency in the adsorption of the studied amines compounds. Different effective parameters on the extraction have been optimized and 15 min extraction time, 10 °C extraction temperature, 300 °C desorption temperature, 5 min desorption time and 100 mL vessel were selected. Construction of the fiber was simple and completed in 5 min. Fiber-to-fiber repeatability was excellent (<8%).

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