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Head space single-drop microextraction of pyridine from nargile smoke and determination by high-performance liquid chromatography

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Abstract
This study aimed to apply the headspace single-drop microextraction (HS-SDME) method for extracting and determining pyridine in nargile smoke samples, followed by high-performance liquid chromatography (HPLC). We optimised the different parameters to evaluate the HS-SDME process. The optimum conditions were 2.5 µL of toluene as the extracting solvent, 150 s as the optimal extraction time, ionic strength of 15% NaCl and stirring of the solution at 700 rpm. Under the optimal conditions, the HS-SDME–HPLC technique has a linear range for pyridine between 0.05 and 30.0 µg L^{-1}, with a minimum limit of detection (LOD) of approximately 0.028 µg L^{-1}. Statistical data showed good accuracy and precision. The proposed method can be used for microextraction and analyses of ultra-trace amounts of pyridine in nargile smoke samples.

Keywords Headspace · Single-drop microextraction · HPLC · Nargile smoke · Pyridine

Abbreviations

DI	Direct immersion
HS	Headspace
LPME	Liquid-phase microextraction
SDME	Single-drop microextraction
UV	Ultraviolet

Introduction

Pyridine is relatively highly toxic and is particularly hazardous to the human body. Cigarette smoke and nargile smoke contain hundreds of toxic compounds, including pyridine and its derivatives. Pyridine affects the human body, causing an increased heart rate and blood pressure, stroke and even lung cancer. Pyridine is the most harmful compound that can affect human health. When pyridine is in the air, it may remain for several months to years. Pyridine mixes very easily with water. It may break down in a few days to a few months when released into water or soil. Pyridine can enter the human body by breathing in the air or smoking cigarettes, drinking contaminated liquid, eating food containing it, especially canned food or contact with the skin. When pyridine enters the body within 1 day, most of the pyridine is absorbed instead of removed from the body by urine. The presence of this toxic compound in cigarette smoke is the most important factor for its analysis and quantification [1]. Several techniques are available for the quantification and detection of pyridine in different samples, such as precipitation [2], gas chromatography [3, 4], high-performance liquid chromatography [5–7] and gas chromatography–flame ionisation detector [8, 9]. Several sample preparation techniques for liquid-phase microextraction (LPME) are used in the aqueous phase to improve detection limits and increase the sample concentration and purification, using a few microliters of extracting solvent. Therefore, pyridine and its derivatives in real samples, such as urine [1], the air inside and around factories, hazardous waste sites in industrial areas [10], food cans and smoke, can be determined and quantified by LPME techniques, such as dispersive liquid–liquid microextraction [11–13] and hollow-fibre liquid-phase microextraction [14, 15]. Single-drop microextraction (SDME) is one of the simplest techniques for liquid-phase microextraction. It uses less than 3 µL, like the extraction phase, which suspends above the syringe used for liquid and gaseous

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samples. Then, after extraction, it can be directly injected into instruments, such as a gas chromatograph or HPLC, for quantitative and qualitative analysis [16]. Generally, it involves two types of single-drop microextraction (direct immersion-SDME (DI-SDME) and headspace-SDME (HS-SDME)). The DI-SDME method can quantify semi-volatile organic compounds in sample matrixes. However, DI-SDME is not widely used because it has limitations, such as difficulties in automation, co-extraction of semi-volatile compounds and the requirement of a pre-transfer step for analytes [17, 18]. HS-SDME was used for the first time in 2001 [19], and the solvent selection of the extraction phase in HS-SDME must be selected according to the vapour pressure. When the vapour pressure of the extracting solvent decreases, the enrichment factor increases under given experimental conditions. In recent years, one of the most important points in HS-SDME has been its application to extract semi-volatile and volatile organic compounds directly in a real sample without any pretreatment step [20]. HS-SDME has several applications for desired volatile compounds; however, its application to semi-volatile analytes is more difficult. HS-SDME can extract volatile organic components from different volatile organic acids [21], aliphatic amines [22], volatile aromatic compounds [23] and medicinal plants [24]. Meanwhile, the application of SDME is limited to non-volatile compounds due to the poor stabilisation of droplets [25, 26]. In this study, the HS-SDME technique was applied for the first time for the extraction of pyridine, as well as the first analysis of pyridine in nargile smoke. Additionally, quantification of the extracted pyridine was performed via the HPLC–UV technique.

Experimental

HPLC conditions

The chromatographic analysis was performed on an HPLC (Knauer) system with a manual injector. Separation was carried out on a C_{18} column (250 × 4.6 mm, with 5.0-µm particle size) from Macherey–Nagel. The mobile phase included solvent A (an aqueous 30 mM phosphate buffer solution at pH 7.4 containing 5.0 mM triethylamine) and solvent B (acetonitrile). The gradient elution programme was 90: 10 (v: v, solvent A: solvent B), followed by a linear gradient to 30: 70 (v: v, solvent A: solvent B) for 5.0 min, and this mixture was held for 1.0 min. Then, the initial conditions were re-established in 1.0 min and held for 5.0 min at a flow rate of 0.8 mL min^{-1}. The injection volume was 20 µL for all samples, and the detection was performed at a wavelength of 254 nm.

Chemicals and materials

Pyridine and triethylamine were purchased from Sigma (St. Louis, MO, USA). HPLC-grade water and acetonitrile were purchased from ParShimi Company (Mashhad, Iran) to prepare the mobile phase. Toluene, xylene, methanol, hydrochloric acid and cyclohexane were purchased from Biochem Company (France) in analytical grade. The stock solution (1000 mg L^{-1}) of pyridine was prepared in methanol and stored at − 4 °C far from light. Working standard solutions were prepared by diluting the above stock solution with HPLC-grade water.

Sampling method

For the preparation of the samples, nargile smoke was directly pumped at 15.0 mL min^{-1} (vacuum compressor pump, D/351 VM, England) for 1 h via trapping, which contained 20 mL (5.0% (v/v) HCl). After sampling, deionised water was added to bring the volume to 100 mL.

Methods

A 25-µL syringe (Hamilton–Bonaduz, Schweiz, Switzerland) was used to perform the HS-SDME experiments. A sample (10 mL) in a conical flask was placed on a magnetic stirrer hotplate (MHS-A, China). Then, 2.5 µL of organic toluene solvent was drawn into the syringe. The tip of the microsyringe distance from the surface of the sample solution was approximately 1.0 cm. Then, the plunger was pressed to cause the solvent to form a 2.5-µL drop suspended from the needle tip. We added 1.5 g of NaCl salt to the solution. Then, the hotplate was heated to 60 °C and stirred at 700 rpm for 150 s during the extraction. The extracting solvent was retracted into the syringe. After the extraction, the solvent in the syringe was mixed well and diluted to 1.0 mL using methanol.

Results and discussion

Optimisation of the HS-SDME procedure

Several factors can affect the extraction efficiency in HS-SDME, such as the nature of the analytes to be extracted, selected extracting solvent, size of the microdrop, extraction time, extraction temperature and ionic strength of the aqueous solution containing the analytes [27]. The selection of an extracting solvent for HS-SDME depends on many factors, such as the need for a high extraction efficiency of analytes of interest, suitable viscosity for

stability of the drop at the top of the syringe for long periods of extraction time and suitable boiling point to avoid losses by evaporation during heating. Furthermore, it must be compatible with the determination system to be used, for example, a chromatographic system in which the extracting solvent should not overlap the detection of analytes in absorption, or it should not interfere with co-elution [28]. The sample volume was fixed at 10 mL for further studies. Additionally, the pH of all sample solutions was adjusted to 11 for subsequent analyses. The pH of the sample solution is important to keep the ionisable basic compounds in their completely deprotonated form for efficient extraction. The best result was obtained at a pH of 11. The experimental variables were tested factor-by-factor to determine the optimal conditions.

Effect of extracting solvent

Different organic compounds, such as toluene, xylene and cyclohexane, were tested as extracting solvents with a microdrop size of 2.0 µL for each solvent, an extraction temperature of 55 °C, ionic strength of 5.0% NaCl, 700 rpm and an extraction time of 120 s. Figure 1 shows the extraction efficiency of pyridine using different solvents. Toluene was finally selected for this study because its extraction efficiency of pyridine is high, and the stability of the microdrop on the top of the syringe during the required time is high compared to other solvents, the stability of the microdrop depends on the viscosity and volatility of drop. In addition, the viscosity of toluene is more stable for producing a drop for long periods and is compatible with HPLC and the UV detector.

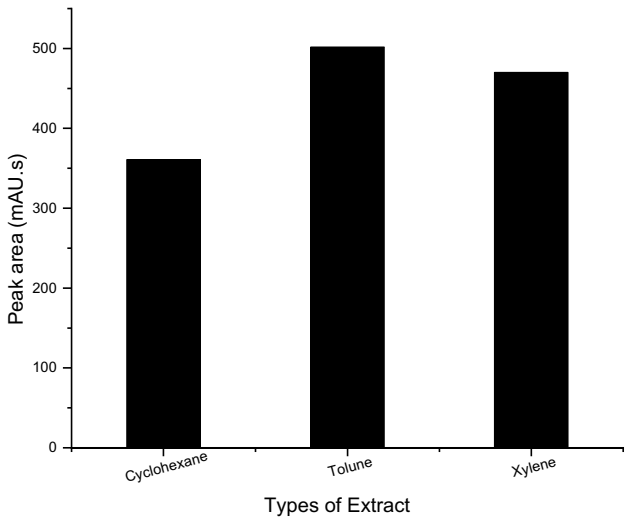

Fig. 1 Effect of different extracting solvents on the extraction efficiency of pyridine

Effect of extracting solvent volume

The drop volume of toluene was optimised from 1.0 to 3.0 µL for an extraction temperature of 55 °C, ionic strength of 5.0% NaCl at 700 rpm and an extraction time of 120 s. The extractant volume increased from 1.0 µL to 2.5 µL. The extraction efficiency of pyridine increased from a peak area of 360 mAU.s to 545 mAU.s, as shown in Fig. 2. Additionally, 2.5 µL for the microdrop of toluene was selected as the optimal volume because increasing the volume of the headspace of the single drop causes instability in the drop size and falling during the extraction period. The volume of microdrop should be the range typically employed in SDME–HPLC applications [29].

Effect of extraction time

The HS-SDME technique requires equilibration to determine the maximum extraction efficiency of pyridine. The effect of extraction time was tested in the range of 30 – 150 s for a micro drop volume of 2.5 µL of each extracting solvent, an extraction temperature of 55 °C, ionic strength of 5.0% NaCl and 700 rpm. As a result, the extraction efficiency was increased by increasing the extraction time, as shown in Fig. 3. Therefore, 150 s was selected as the optimum extraction time for further experiments. The techniques cannot be applied when drop stability decreases [30]. Thus, this technique cannot be applied for more than 150 s.

Effect of temperature

The temperature can affect the kinetics and thermodynamics of the HS-SDME of volatile and semi-volatile compounds [31]. In this case, increasing temperature increases the extraction in HS-SDME. Figure 4 shows that the

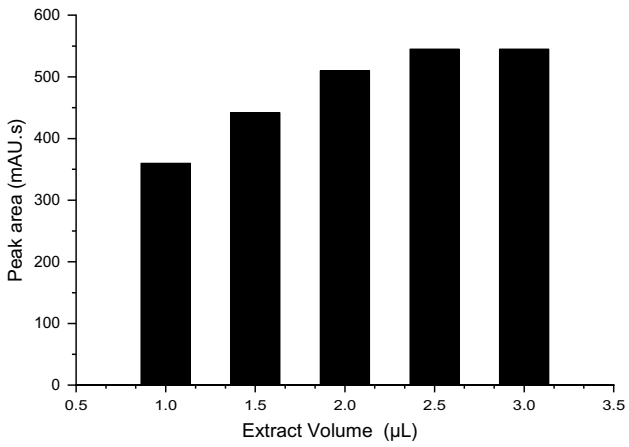

Fig. 2 Effect of the toluene volume (extracting solvent) on the extraction efficiency of pyridine

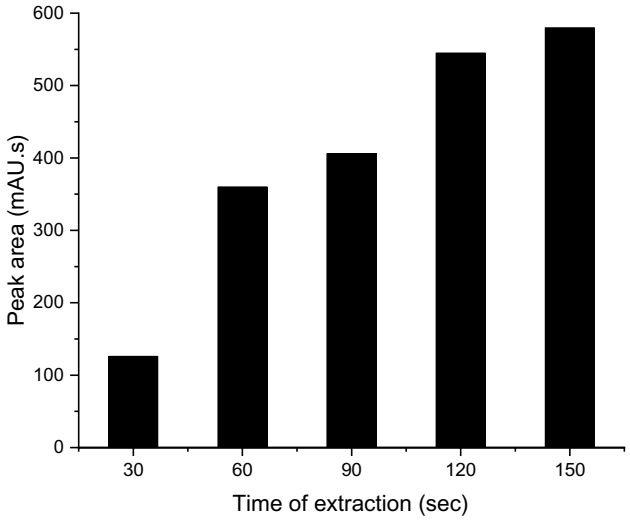

Fig. 3 Effect of the time of extraction solvent on the extraction efficiencies of Pyridine

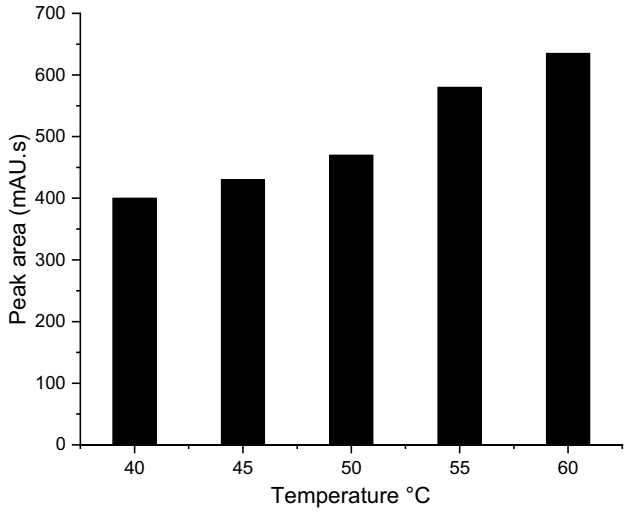

Fig. 4 Effect of temperature of extracting solvent on the extraction efficiency of pyridine

temperature range of 40 to 60 °C was examined. As a result, 60 °C was selected as an optimum temperature to determine the maximum extraction efficiency of pyridine. Despite this, we could not examine this technique above 60 °C because increased temperature affects the sorption process, which causes a decrease in the partition coefficients of the analytes. This decreases the stability of the drop during extraction from the aqueous phase to the microdrop of the organic phase [32].

Effect of ionic strength

The effect of the ionic strength of the solution on the extraction efficiency of pyridine was examined from 0.0 to 25.0% NaCl for a micro drop size of 2.5 µL of toluene, an extraction temperature of 60 °C and an extraction time of 150 s. Then, we selected 15% NaCl as the optimal condition. The results indicated a considerable effect of ionic strength on the extraction efficiency of pyridine, which has higher water solubility. Due to the salting-out effect, an increase in the ionic strength of the sample solution leads to a decrease in the solubility of the analyte and consequently increases the partition of analytes into the organic (gas) phase [33]. In the study, NaCl was used for salting out.

Effect of stirring

The effect of stirring the solution on the extraction efficiency of pyridine was also studied, which was tested from 0.0 to 1000 rpm for a microdrop size of 2.5 µL of toluene, an extraction temperature of 60 °C, an extraction time of 150 s and 15.0% NaCl as the ionic strength of the solution. The optimal result occurred at 700 rpm, which was used for further studies.

Application

Table 1 shows the results of pyridine extraction, determination and accuracy from nargile smoke samples. This study showed the practical applicability of the proposed method under optimised conditions for the quantification of pyridine.

Table 1 Results of the extraction, determination and accuracy of pyridine in nargile smoke samples

Sample	Added pyridine (µg L^{-1})	Found (µg L^{-1})	Found from 1.0 h smoking (µg)	RR%	E* %
Sample 1 (lemon flavour)	0	464	46.4	96.14	−3.86
	725	1161		96.84	−3.16
	2500	2885			
Sample 2 (apple flavour)	0	523	52.3	93.52	−6.48
	725	1201		98.72	−1.28
	2500	2966			

*$n = 3$ replicate

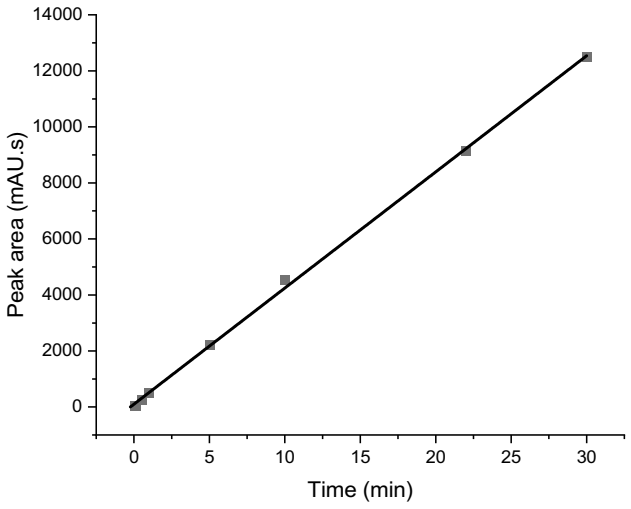

Fig. 5 Calibration curve of standard pyridine solution

Table 2 Statistical characteristics of the proposed (HS-SDME–HPLC) method for determining pyridine

Parameter	Characteristic
Regression equation	$y=a+b*x$
Intercept (a)	100.64 ± 61.96
Slope (b)	414.62 ± 4.51
Correlation coefficient (r)	0.9997
Coefficient of determination (r^2)	0.9993
Linear range μg L^{-1}	0.05 to 30.0
Limit of detection (LOD) μg L^{-1}	0.028
Limit of quantification (LOQ) μg L^{-1}	0.083

The relative recovery (RR%) was calculated by the following Eq. (1):

$$RR\% = \frac{C_{found} - C_{real}}{C_{added}} \times 100 \quad (1)$$

where C_{found} is the concentration of analyte after adding a known amount of standard into the real sample. C_{real} is the concentration of analyte that initially was present in the real sample, and C_{added} is the concentration of the known amount of standard spiked in the real sample. The relative errors (%) were calculated using Eq. (2).

$$Relativeerror(E\%) = RR\% - 100 \quad (2)$$

The linear range of pyridine was between 0.05 and 30.0 μg L^{-1}, and the calibration curve is shown in Fig. 5. The LOD was 0.028 μg L^{-1}, and LOQ was approximately 0.083 μg L^{-1}. The correlation coefficient was 0.9997, and the sensitivity was 414.62 mAU.s/μg L^{-1}. The data are summarised in Table 2. To show the repeatability of the proposed method, we measured five replicated peak heights of pyridine at a concentration of 1.0 μg L^{-1}, and the relative standard deviation (RSD%) of pyridine was found to be 3.06%. Figure 6 shows the HPLC chromatograms of a standard 1.0 μg L^{-1} of pyridine solution and chromatograms of nargile smoke samples after pyridine extraction under the optimal experimental conditions. The pyridine peak appeared at the retention time of 6.05 min. The results of this method indicated good performance for determining pyridine in nargile smoke samples.

White analytical chemistry

White analytical chemistry (WAC) stems from green analytical chemistry. WAC involves 12 principles, which are key criteria affecting the quality of the method: analytical (red), practical (blue) and environmental impact (green). WAC

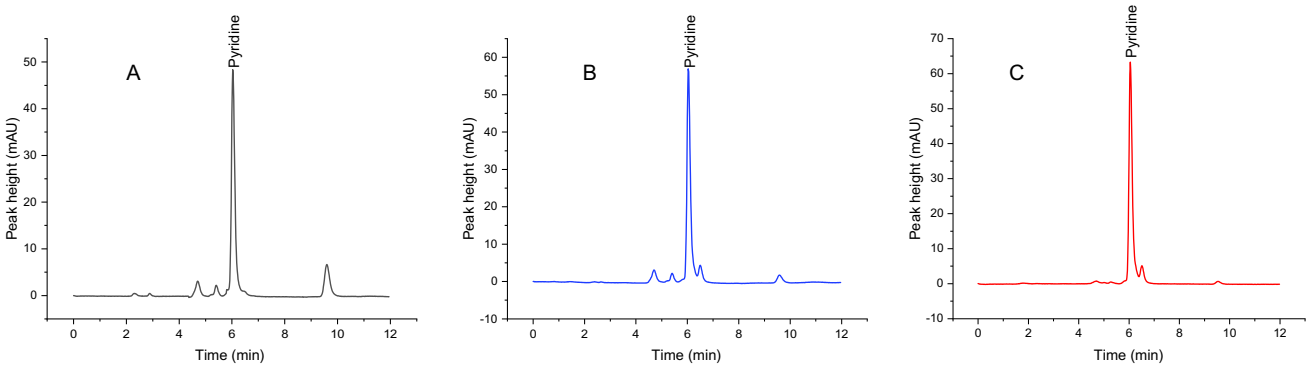

Fig. 6 **a** Typical HPLC chromatogram of 1.0 μg L^{-1} of pyridine standard solution, **b**, **c** HPLC chromatograms of nargile smoke samples (1 and 2) under optimal experimental conditions, respectively

Table 3 Comparison between the present study results and other methods

Analytical method	Extraction	Sorbent	Matrix	Red (R)	Green (G)	Blue (B)	Ref
HPLC	Electrical field-stimulated liquid-phase microextraction	Hollow fibre-supported liquid membrane	Cigarette	76.25	63.75	63.75	[36]
HPLC	Ultrasound-assisted emulsification microextraction	1-hexanol	Smokers' urine	60	57.5	73.75	[35]
HPLC	HS-SDME	Toluene	Nargile smoke	95	85	81.25	Present work

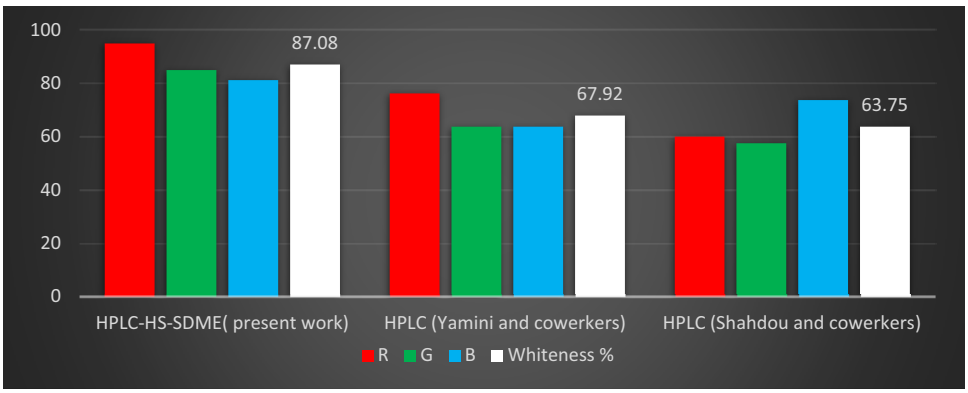

Fig. 7 Comparison of the three methods for determining pyridine according to the 12 principles of WAC

is closer to sustainable development due to its complete view, as it strives for a compromise that avoids an unconditional increase in greenness at the expense of functionality [34]. The data show a comparison of the three methods for determining pyridine (Table 3). The overall assessments, expressed by the WAC parameter, yielded different results from those obtained by Shahdou and coworkers in 2015 (63.75%) [35], Yamini and coworkers in 2015 (67.92%) [36] and (87.08%) those of the present study, indicating that the analysed methods have different potentials for pyridine determination, as shown in Fig. 7. The greenness percentage of HS-SDME is more than that of other methods.

Conclusions

In this study, the HS-SDME–HPLC technique was successfully applied to extract and determine pyridine in nargile smoke samples. An acidic trap sampling system for trapping pyridine in nargile smoke was employed. This method is greener and more eco-friendly than others methods to determination of pyridine according to the WAC method. As a result, it is better than others due to high blue and green parameters. HS-SDME–HPLC also has a high red parameter because of very low LOD and LOQ and a good calibration curve range. Because it uses low amounts of organic solvents for extraction (microliters), only a short extraction time is required (only 2.5 min). Under the optimum conditions, the HS-SDME–HPLC technique has good accuracy and precision and has a minimum LOD of approximately 0.025 µg L^{-1}. This method was successfully applied to the analysis of pyridine in nargile smoke from two types of common nargile [lemon flavour (sample−1) and apple flavour (sample-2)], which contain 46.4 and 52.3 µg of pyridine, respectively, when nargile is smoked for 1.0 h. This method can be used for microextraction and analysis of pyridine in different samples at ultra-trace levels.

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