

Article

Deep Eutectic Solvent-Based Coating Sorbent for Preconcentration of Formaldehyde by Thin-Film Solid-Phase Microextraction Technique

Justyna Werner ^{*}, Agnieszka Zgoła-Grzeskowiak  and Tomasz Grzeskowiak

Institute of Chemistry and Technical Electrochemistry, Faculty of Chemical Technology, Poznan University of Technology, Berdychowo 4, 60-965 Poznan, Poland; agnieszka.zgola-grzeskowiak@put.poznan.pl (A.Z.-G.); civ@tlen.pl (T.G.)

* Correspondence: justyna.werner@put.poznan.pl

Abstract: A thin-film solid-phase microextraction method with a sorbent composed of a deep eutectic solvent was developed for the preconcentration of formaldehyde from river and lake water samples. Four new deep eutectic solvents (DESs) were synthesized, each in molar ratios 1:1, 1:2, and 1:3. Among prepared compounds, the greatest efficiency in the proposed method of preconcentration of formaldehyde derivatized with Nash reagent was demonstrated by DES-3 consisting of benzyltrimethylhexadecylammonium chloride and lauric acid, in a molar ratio of 1:3. For the proposed method, the parameters affecting the extraction efficiency of formaldehyde were optimized (including the choice of DES-based sorbent and desorption solvent as well as the sample volume and pH, the salting-out effect, the extraction time, and the desorption time). Under optimal conditions, the proposed method achieved good precision between 3.3% (for single sorbent) and 4.8% (for sorbent-to-sorbent) as well as good recovery ranging from 78.0 to 99.1%. The limits of detection and quantitation were 0.15 ng mL⁻¹ and 0.50 ng mL⁻¹, respectively. The enrichment factor was equal to 178. The developed method was successfully applied to determine formaldehyde in environmental water samples.

Keywords: benzyltrimethylhexadecylammonium chloride; lauric acid; deep eutectic solvent; formaldehyde; thin-film solid-phase microextraction



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1. Introduction

Formaldehyde occurs naturally in the environment. Most organisms produce it in small amounts during their metabolism and it is also a by-product of combustion and other natural processes. Formaldehyde is also a product of anthropogenic activities such as burning fuel, residential wood burning, and smoking tobacco [1]. However, for many years, formaldehyde has been also applied in industries mainly with antimicrobial action. Therefore, it is commonly used as a fungicide, germicide, disinfectant, and preservative in medical laboratories [1,2]. Formaldehyde is also widely used as a chemical solvent, raw material for the production of resins, wood fixatives as well as paper and pulp production, cosmetics, food, and the textile industry. Such a variety of applications of formaldehyde affects its continuous presence in the environment [1,3].

Formaldehyde is toxic for people, causes irritation of the eyes and respiratory tract, headaches, nausea, drowsiness, and allergic skin reactions [2–4]. It is considered by the International Agency for Research on Cancer (IARC) as a carcinogen as well as classified by the Environmental Protection Agency (EPA) as a probable human carcinogen (the EPA's B1 classification). Most of the research on the carcinogenicity of formaldehyde focuses on chronic respiratory exposure because this is the main way of industrial and household exposure [4,5].

Over the years, analytical methods based mainly on high-performance liquid chromatography [6–12], gas chromatography [13–16], spectrophotometry [17–19], and spectrofluorimetry [20] have been developed to determine formaldehyde in different kinds of samples. However, the direct determination of formaldehyde is complicated owing to its volatility, high polarity and chemical reactivity, as well as lack of a chromophore (or a fluorophore). Derivatization successfully solves these problems. Different reagents such as 2,4-dinitrophenylhydrazine (DNPH) [6–8,11–13], O-2,3,4,5,6-(pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) [15,16,21], and Nash reagent (prepared by mixing acetylacetone, acetic acid and ammonium acetate) [9,14,17–19,22] have been most often used for the derivatization of formaldehyde.

Sample preparation often includes preconcentration of analytes and is considered an essential part of analytical methods. Therefore, for the isolation and preconcentration of trace amounts of formaldehyde different techniques are used such as liquid-phase microextraction (LPME) [6,10,11], ultrasound-assisted emulsification microextraction (USAEME) [17], dispersive liquid-liquid microextraction (DLLME) [7–9,12,18,19,22], single drop microextraction (SDME) [13,20] and solid-phase microextraction (SPME) [14–16,21,23].

SPME is an established analytical technique and relies on analyte isolation with a sorbent-coated fiber [24]. The fiber is fixed in the needle that is exposed to a sample to adsorb analytes that are subsequently desorbed thermally directly into a gas chromatograph or using solvent when high-performance liquid chromatography is to be used [25,26]. Extraction in SPME is based on the partition equilibrium of the analytes between a sample and a fiber combining extraction and preconcentration into a single step [25,27]. Because this technique can be easily used for sample preparation in the determination of trace amounts of analytes, many studies have been performed aiming at an increase of the extraction efficiency by using different sorbents and different geometries of supports [26–29]. Thin-film SPME was introduced as a new geometry of SPME in 2003 [30]. It takes the advantage of a greater sorbent volume with a more developed surface area allowing to gain bigger sensitivity [31]. In the present study, a stainless steel mesh support is proposed that enables the deposition of a large sorbent mass.

Current studies on the improvement of the SPME technique often propose new coating materials, which may lead to the improvement of the extraction process taking advantage of their high selectivity, thermal and mechanical resistance as well as multiple uses. As a result, commercially available SPME sorbents including polydimethylsiloxane (PDMS), polyacrylate (PA), divinylbenzene (DVB) in some applications may be replaced by metal-organic frameworks (MOFs), molecularly imprinted polymers (MIPs), magnetic nanoparticles (MNs), ionic liquids (ILs) [26,27]. In this paper, a new coating sorbent based on a deep eutectic solvent (DES) is proposed.

DESs can be synthesized by mixing hydrogen bond acceptors (HBAs) with hydrogen bond donors (HBDs). Their properties resemble ionic liquids, but they are cheaper, often less toxic, non-flammable, biodegradable and easier to synthesize without any purification [32,33]. DESs may be used as extractants in liquid-phase microextractions [34]. Nevertheless, their usage in SPME is limited as there are only a few publications presenting modifications of popular SPME sorbents with these compounds. This may be caused by weak mechanical stability resulting in low reproducibility. Our research team recently prepared DES based on trihexyl(tetradecyl)-phosphonium chloride and n-docosanol to preconcentrate parabens in surface waters [35].

In this study, a DES sorbent was applied to the mesh support and used for preconcentration of formaldehyde (after derivatization) from the environmental water samples.

2. Materials and Methods

2.1. Reagents and Solutions

The reagent used in this study were of analytical grade and were applied without purification. HPLC-grade water was prepared by reverse osmosis, followed by double distillation. A stock solution of formaldehyde ($400 \mu\text{g mL}^{-1}$) was done by diluting 37%

(*v/v*) formaldehyde (Merck, Darmstadt, Germany). Glacial acetic acid (Reagent Plus, $\geq 99\%$, Sigma-Aldrich, Poland), ammonium acetate (purity $\geq 98.0\%$, Avantor Performance Materials, Poland) and acetylacetone (purity $\geq 99.0\%$, Merck) were applied for formaldehyde derivatization in the Hantzsch reaction. Benzyltrimethylhexadecylammonium chloride (purity $\geq 98.0\%$), trihexyl(tetradecyl)phosphonium chloride (purity $\geq 95.0\%$), lauric acid (purity $\geq 98.0\%$) were purchased from Sigma-Aldrich and 1-docosanol (purity $\geq 98.0\%$) was bought from Merck. Sodium chloride (purity 99.99% Suprapur[®], Merck) was used to check the ionic strength effect. Sodium hydroxide solution (30%, Suprapur[®], Merck) and hydrochloric acid (30%, Suprapur[®], Merck) after proper dilution were applied for adjusting the pH of the samples. Acetonitrile (gradient grade for LC, LiChroSolv[®]) and methanol (gradient grade for LC, LiChroSolv[®]) were bought from Merck and applied for both desorption of the derivatized formaldehyde and its chromatographic determination.

2.2. Real Samples

The samples of the lake (Malta Lake, Baba Lake, Kórnickie Lake) and river (Cybina River, Warta River) water were collected in Greater Poland into plastic bottles. They were stored at $-18\text{ }^{\circ}\text{C}$ until analysis and directly before sample preparation they were warmed to room temperature and filtered.

2.3. Equipment and Measuring Apparatus

The thin-film solid-phase microextraction (TF-SPME) support made from stainless steel mesh was bought from Ann Filters (Poland). A magnetic stirrer (SunLab SU1300, Aschaffenburg, Germany) was used to synthesize DESs. A pH-meter (EL20, Mettler Toledo, Greifensee, Switzerland) equipped with the LE407 electrode was applied for controlling pH. An orbital shaker (PSU-20i, Grant-Bio, Keison Products, Chelmsford, UK) set to handle bottles of up to 250 mL capacity was used for extraction. An HP 1100 chromatographic system (Hewlett Packard, Palo Alto, CA, USA) equipped with a UV-Vis detector was applied for the determination of formaldehyde. The system was controlled by the ChemStation software from the same company. A Zorbax[®] ODS column (150 mm \times 4.6 mm I.D., 5 μm particles) from Agilent (Santa Clara, CA, USA) was used in the analysis. The Fourier-transform infrared spectroscopy (FT-IR) allowed for the recording of spectra of the sorbent prepared from DES. The analysis was done using the IFS 66v/S FT-IR spectrometer from Bruker Optic (Ettlingen, Germany). Scanning was done in the reflection mode using the attenuated total reflection (ATR) module from Perkin Elmer (Waltham, MA, USA). The samples underwent scanning from 500 to 4000 cm^{-1} . The morphology of the sorbent on the mesh support was studied using a scanning electron microscope (SEM, S-3400N, Hitachi, Japan). For better quality of the images, the Cressington Carbon Coater was used which enabled coating the surface of studied materials with conductive carbon material. A tungsten wire cathode working at the acceleration voltage of 0.3 to 30 kV served as the primary electron beam source. The range of magnification was from 5 to 300,000 \times with a resolution of 3.0 nm for secondary electron image (30 kV acceleration voltage, in high vacuum mode), 10 nm for secondary electron image (3 kV acceleration voltage, in high vacuum mode), 4.0 nm for backscattered electron image (30 kV acceleration voltage, in low vacuum mode). The NSS spectral imaging software (Thermo Scientific, Waltham, MA, USA) was applied to perform the elemental analysis using the Energy Dispersive X-ray Spectrometry technique (EDS).

2.4. Synthesis of DES-Based Sorbents

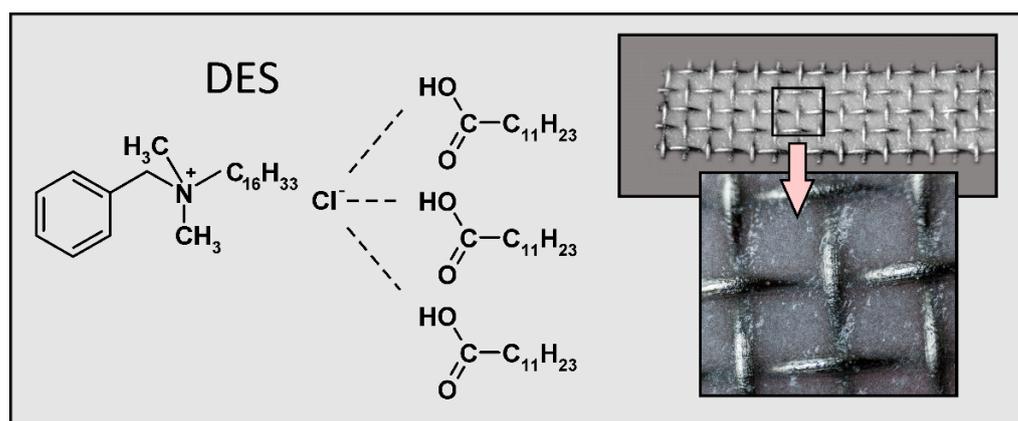
DES-1, DES-2, DES-3 and DES-4 were synthesized by weighing the appropriate amounts of HBD and HBA in 1:1, 1:2 and 1:3 molar ratios, each of them into a flat bottom flask. Then, mixtures were heated at $90\text{ }^{\circ}\text{C}$ with continuous stirring for 20 min until homogeneous liquids were obtained. Upon cooling to room temperature, the prepared DESs were solidified. The structures of all the synthesized DESs are presented in Table 1.

Table 1. Structures of DES-based coating sorbents composed of HBA and HBD in different molar ratios.

DES	HBA:HBD (Molar Ratio)	Structure of HBA	Structure of HBD
DES-1	1:1	$\text{H}_3\text{C}(\text{H}_2\text{C})_5\text{-P}^+\begin{matrix} (\text{CH}_2)_5\text{CH}_3 \\ \\ (\text{CH}_2)_5\text{CH}_3 \end{matrix} \text{Cl}^-$	$\text{C}_{11}\text{H}_{23}\text{COOH}$
	1:2		
	1:3		
DES-2	1:1	$\text{H}_3\text{C}(\text{H}_2\text{C})_5\text{-P}^+\begin{matrix} (\text{CH}_2)_5\text{CH}_3 \\ \\ (\text{CH}_2)_5\text{CH}_3 \end{matrix} \text{Cl}^-$	$\text{C}_{22}\text{H}_{45}\text{OH}$
	1:2		
	1:3		
DES-3	1:1	$\text{C}_6\text{H}_5\text{-CH}_2\text{-N}^+\begin{matrix} \text{CH}_3 \\ \\ \text{CH}_2(\text{CH}_2)_{14}\text{CH}_3 \\ \\ \text{CH}_3 \end{matrix} \text{Cl}^-$	$\text{C}_{11}\text{H}_{23}\text{COOH}$
	1:2		
	1:3		
DES-4	1:1	$\text{C}_6\text{H}_5\text{-CH}_2\text{-N}^+\begin{matrix} \text{CH}_3 \\ \\ \text{CH}_2(\text{CH}_2)_{14}\text{CH}_3 \\ \\ \text{CH}_3 \end{matrix} \text{Cl}^-$	$\text{C}_{22}\text{H}_{45}\text{OH}$
	1:2		
	1:3		

2.5. Preparation of Supports with DES-Based Sorbents

A stainless steel mesh was cut into 15.0 cm × 0.7 cm strips and used as a support for the coating sorbent. The surfaces of mesh supports were cleaned in acetonitrile (ACN) for 1 h prior to use. The DES-based sorbents were applied to the mesh support in the form of a thin film by the dip-coating method. DES was heated to a temperature of 70 °C (at which it was liquid) and then the mesh support was immersed in it to a height of 2.9 cm (the height of 18 mesh). The excess sorbent was removed, so that it only filled the mesh, thus allowing for obtaining thin layers of DES about a similar area. After a few seconds, when DES cooled down and solidified on the mesh support, a sorbent with a constant and repeatable surface was obtained (Figure 1). Before and after coating the mesh support was weighed. Next, the mass of the material on the support was calculated, which varied from 42.3 to 43.1 mg.

**Figure 1.** The structure of synthesized DES and its photography.

2.6. Derivatization of Formaldehyde

The Hantzsch reaction is a known cyclization reaction of acetylacetone and formaldehyde in the presence of ammonium ions (Figure 2). It is a method of formaldehyde derivatization forming a less volatile, less reactive chromophore—3,5-diacetyl-1,4-dihydrolutidine (DDL). A derivatizing mixture, the so-called Nash reagent, was prepared by dissolving 150 g of ammonium acetate in ultrapure water and adding 3.0 mL of glacial acetic acid and 1.5 mL of acetylacetone, and filling to 1000 mL with water. Nash reagent prepared in this way was poured into a dark glass bottle and was used after 12 h from preparation. Next, to

a glass bottle, 800 mL of previously filtered sample (containing formaldehyde) and 80 mL of Nash reagent were added. The obtained solution was heated at 40 °C in a water bath for 30 min, next cooled to room temperature. During this time, the reaction of formaldehyde derivatization takes place. Derivatization reaction conditions were applied according to ISO 14184-1:2011 [36].

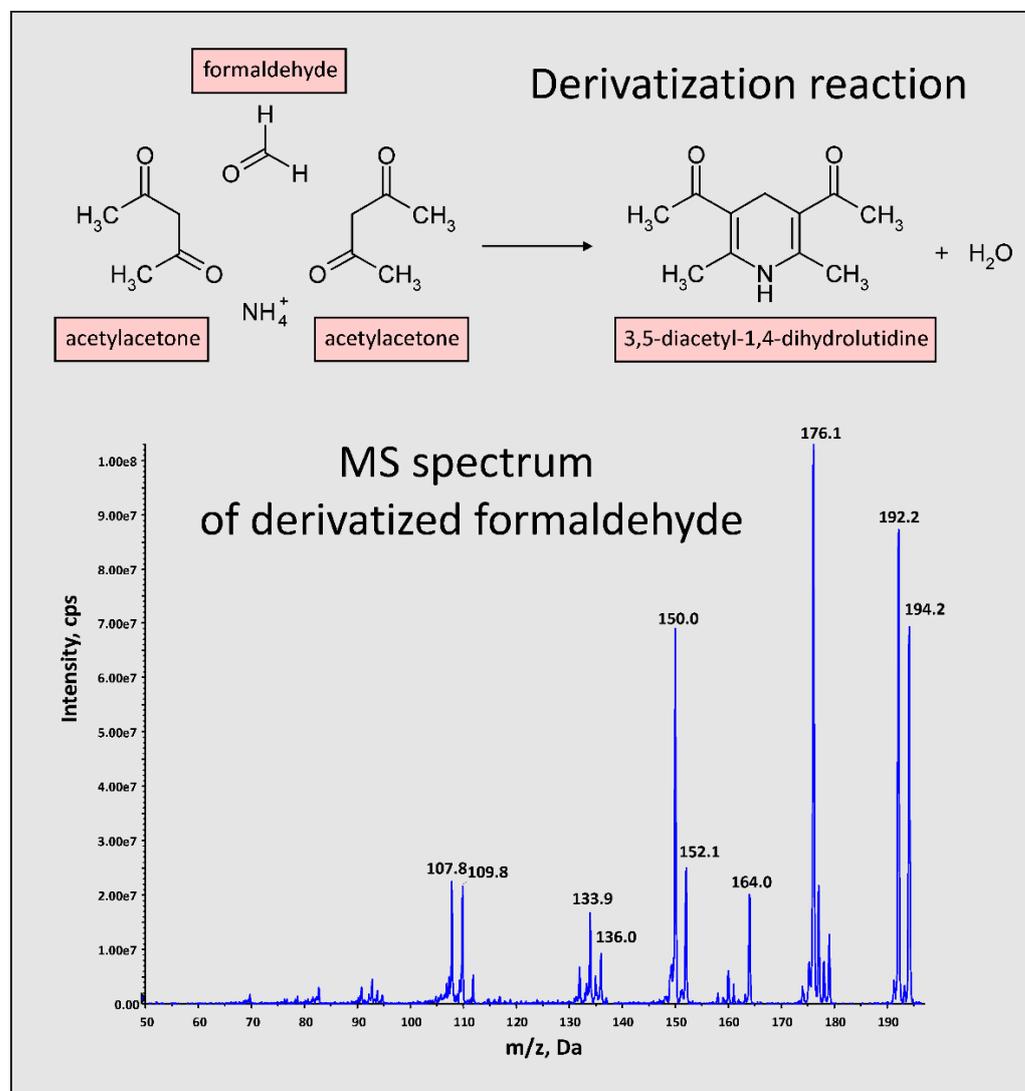


Figure 2. The Hantzsch reaction between Nash reagent and formaldehyde and the mass spectrum of 3,5-diacetyl-1,4-dihydrolutidine formed in the reaction.

2.7. DES-TF-SPME Procedure

While the derivatization of formaldehyde gives the possibility of its determination with the UV detector, the preconcentration adds additional sensitivity. The preconcentration was done as follows. From a bottle with derivatized samples (lake, river or ultrapure water), a 200 mL aliquot was taken and placed in a 250 mL bottle. Then, the samples were brought to pH = 7.0 and 0.03 g mL⁻¹ of NaCl was added (the salting-out effect). The mesh strips coated with DES-3(1:3) sorbent were immersed in the bottle with the sample solution and then the solution was stirred for 20 min at 200 rpm on a shaker to adsorb 3,5-diacetyl-1,4-dihydrolutidine onto the DES sorbent. Next, the sorbent was immersed in 1 mL of acetonitrile/water mixture (9:1, v/v) and mechanically shaken for 8 min at 200 rpm to desorb the formaldehyde derivative. The resulting sample solution was passed through a 0.2 µm Nylon syringe filter before the chromatographic analysis.

2.8. HPLC Conditions

The analysis was performed on an HP 1100 chromatographic system. The sample (10 μL) was injected into the Zorbax[®] ODS column thermostated at 25 °C. The acetonitrile: water (85:15, *v/v*) mobile phase flow rate was 1.0 mL min⁻¹, and the detection was set to 410 nm. For the determination of formaldehyde the external standard method was used.

3. Results and Discussion

DESs that are intended for use as coating sorbents in TF-SPME have to be solid at room temperature and fulfill a few requirements, including insolubility in water and desorption solvents as well as mechanical stability on the support. That is why the synthesis of many DESs was done to find a few appropriate ones meeting the above conditions (Table 1).

3.1. Selection of Sorbent Material and Solvent for Desorption

Both extraction and desorption are very important steps in the development of the SPME method. Therefore, at the very beginning, the selection of the coating sorbent and solvent used for desorption was done simultaneously. One must take into account that an appropriate desorption sorbent is crucial in SPME coupled with HPLC, not only to desorb the analytes but also because it determines the possibility of multiple sorbent usage.

To select the best coating sorbent, DES-1, DES-2, DES-3 and DES-4 (each in molar ratios 1:1, 1:2, 1:3) were tested. The composition of these sorbents indicates their slight polarity which should increase the sorption of derivatized formaldehyde. To select the best desorption solvent, mixtures of methanol/water and acetonitrile/water were used, but desorption in the mixture of methanol/water was much lower compared to desorption in the mixture of acetonitrile/water. For that reason, in the next stage four mixtures were tested that is 90:10, *v/v*, ACN/H₂O; 80:20, *v/v*, ACN/H₂O; 70:30, *v/v*, ACN/H₂O; 60:40, *v/v*, ACN/H₂O.

The mass and thickness were kept almost constant for all coatings. The tests were conducted using a 200 mL sample containing 125 ng mL⁻¹ of formaldehyde (after derivatization) with 0.05 g mL⁻¹ NaCl added, and the extraction time and desorption time were 30 min and 12 min, respectively. Figure 3 shows that the best results were obtained for DES-3(1:3) with a mixture of ACN/H₂O in a ratio of 90:10 (*v/v*) as a desorption solvent. The structure of DES-3 indicates its more polar properties than that of the other tested DESs. It shows that interactions between the analyte and the sorbent may be considerably influenced by their polar nature. Thus, for further tests, DES-3 and ACN/H₂O in a ratio of 90:10 (*v/v*) were selected.

3.2. Characterization of the Selected Coating Sorbent

The FT-IR spectrum of DES-3(1:3) contains characteristic bands: intermolecular hydrogen bonds (3600–3200 cm⁻¹), stretching bands of C-H bonds of hydrocarbon chains (2920 cm⁻¹ and 2851 cm⁻¹), and stretching bands of C-H bonds of CH₃ groups at 2952 cm⁻¹. Moreover, there are bands at 1409 and 1394 cm⁻¹ of the O-H groups of carboxylic acids and a band at 1728 cm⁻¹ characteristic for the C=O bond in carboxylic acids. The band characteristic for the C-N bond occurs at 1083 cm⁻¹, and the band characteristic for C-O occurs at 1161 cm⁻¹. The FT-IR spectrum of DES-3(1:3) is presented in Figure 4.

SEM was used to examine the morphology as well as observe the film thicknesses of the DES-3(1:3) sorbent coated on the support mesh (Figure 5). A fine structure of DES-3(1:3) was found on the stainless steel mesh.

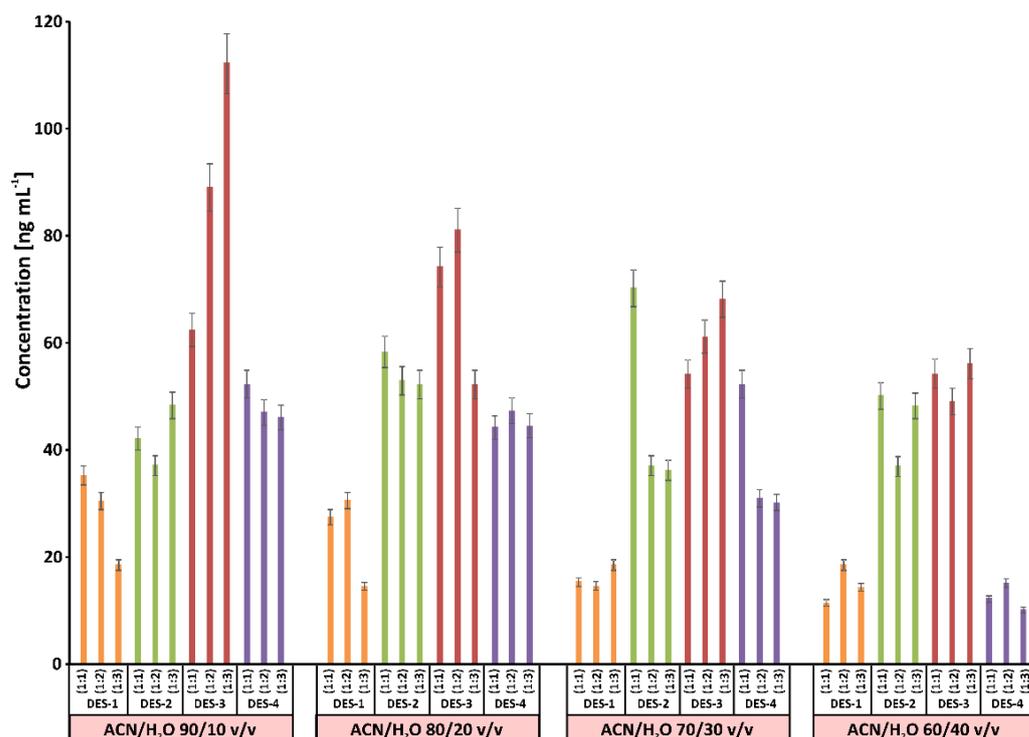


Figure 3. Influence of coating DES-based sorbent prepared with DES-1 (orange), DES-2 (green), DES-3 (burgundy) and DES-4 (violet) each in molar ratios 1:1, 1:2, 1:3 and desorption solvent (ACN/H₂O in different volume ratios) on analytical signals of formaldehyde derivative obtained by the DES-TF-SPME/HPLC-UV-Vis method. The measurements were performed using 200 mL samples containing 125 ng mL⁻¹ of formaldehyde derivative. Conditions: extraction time 30 min with the addition of 0.05 mg L⁻¹ NaCl and desorption for 12 min (*n* = 4).

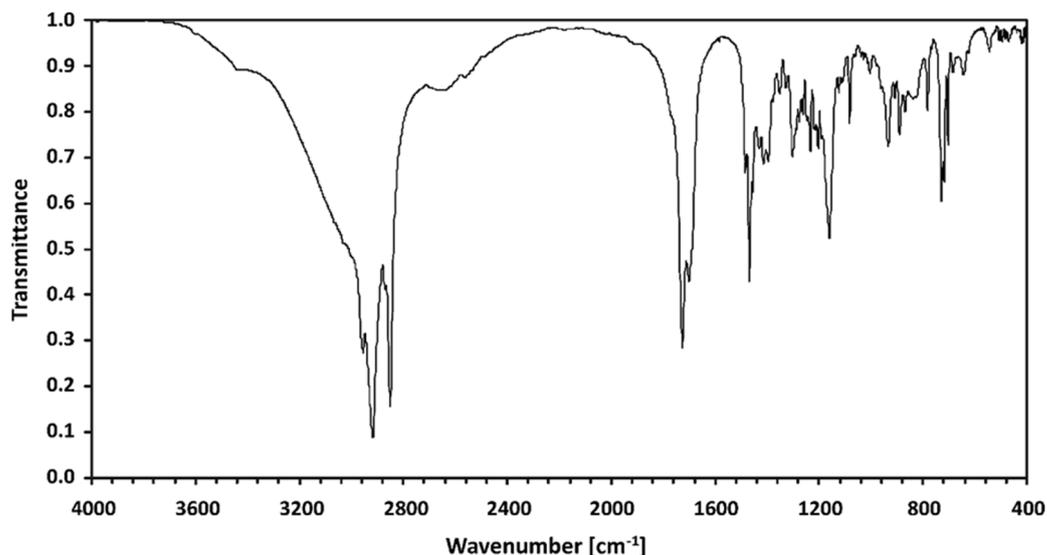


Figure 4. The FT-IR spectrum of DES-3(1:3).

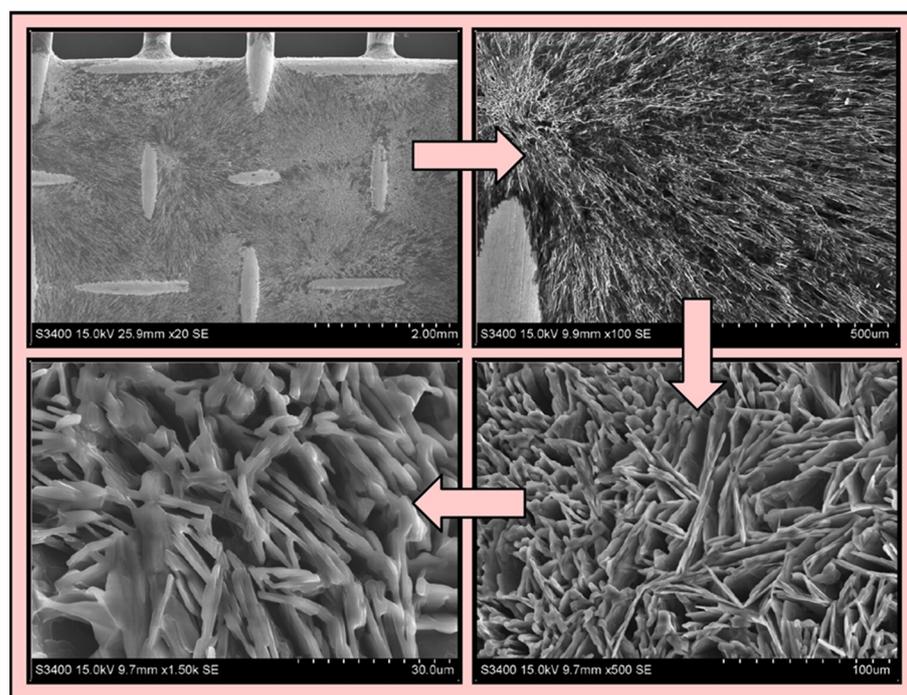


Figure 5. Scanning electron micrographs of the DES-3(1:3) sorbent deposited on the mesh.

Qualitative and quantitative analysis of elements found in DES-coated mesh was performed on the surface of the tested materials (without the use of graphite sputtering). The EDS analysis of DES-3(1:3) enabled to determine the elemental composition of elements, but a precise percentage of particular elements could not be calculated. Even though DES was liquid during its synthesis different percentage of elements was measured on various surface parts after its solidification (Figure 6).

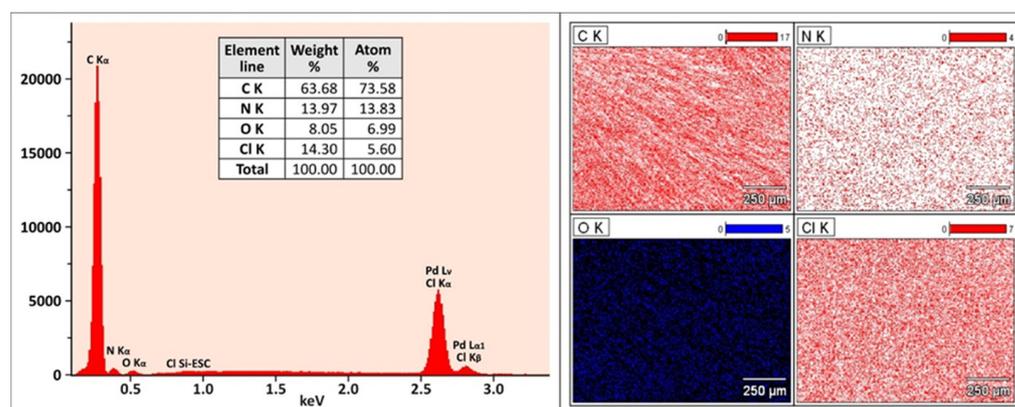


Figure 6. Structures of DES-3(1:3) sorbent confirmed by energy-dispersive X-ray spectroscopy.

3.3. Optimization of DES-TF-SPME Conditions

To obtain a highly effective method for the extraction of formaldehyde, selected factors influencing the analytical signal were examined. Thus, the volume and pH of samples, the salting-out effect, as well as extraction and desorption time were all tested.

3.3.1. Volume of Samples

There are several factors influencing the amount of analyte extracted in SPME including sample volume. Therefore, to evaluate the best sample volume a standard solution containing 125 ng mL^{-1} of formaldehyde (after derivatization) with volumes 100, 150,

200 mL was used. The response for tested formaldehyde was almost equal in that range indicating that the product of distribution constant and sample volume is much greater than the coating material volume. Thus, the extracted quantity of formaldehyde is proportional only to the volume of sorbent. As a result, for further testing, a sample volume of 200 mL was chosen.

3.3.2. The pH of Samples

The extraction efficiency of the formaldehyde derivative may be influenced by the pH of the samples. In the pH optimization stage, changes in sample pH ranging from 3 to 9 were done to test the extraction performance of the DES-based sorbent. The obtained results (Figure 7a) indicate that the optimal pH of the samples is 7. The obtained result is confirmed by the research of Rohyami and Pribadi [37], who found out that 3,5-diacetyl-dihydrolutidine is stable at a neutral pH. At acid conditions, the formation of formaldehyde derivative is reduced while at alkaline pH the derivative is unstable. Furthermore, at alkaline pH, the hydroxyl ions may induce changes in the sorbent material lowering the affinity of the formaldehyde derivative. Based on the obtained results (Figure 6a), in further testing, the samples were brought to pH 7.

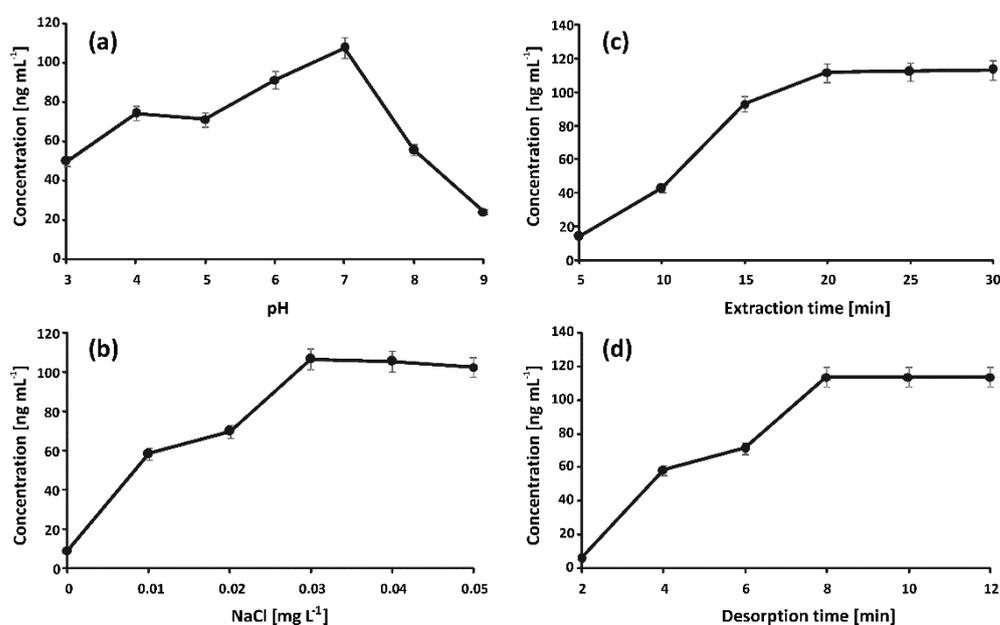


Figure 7. Effect of pH of samples (a), amount of NaCl (b), extraction time (c), and desorption time (d) on the performance of the DES-TF-SPME method. The measurements were performed using 200 mL samples containing 125 ng mL⁻¹ of formaldehyde derivative ($n = 4$). Conditions: (a) Extraction time 30 min with the addition of 0.05 mg L⁻¹ NaCl and desorption with a mixture acetonitrile/water (90/10, v/v) for 12 min. The pH is a variable value. (b) Extraction time 30 min and desorption with a mixture of acetonitrile/water (90/10, v/v) for 12 min. The pH of the sample is adjusted to 7. The amount of NaCl is a variable value. (c) Extraction with the addition of 0.03 mg L⁻¹ NaCl and pH adjusted to 7, desorption with a mixture of acetonitrile/water (90/10, v/v) for 12 min. The extraction time is a variable value. (d) Extraction time 20 min with the addition of 0.03 mg L⁻¹ NaCl and pH adjusted to 7, desorption with a mixture of acetonitrile/water (90/10, v/v). The desorption time is a variable value.

3.3.3. The Addition of NaCl

The improvement of extraction efficiency may sometimes result from the addition of salt to aqueous samples, as this lowers the solubility of the analytes. Therefore, to test the influence of the ionic strength on the extraction yield, sodium chloride was added at concentrations from 0 to 0.05 g mL⁻¹. A gradual increase of the analytical signal was

observed up to 0.03 g mL^{-1} NaCl and then a slight decrease at greater concentrations was found. This decrease may result from the increased sample viscosity slowing down the diffusion of 3,5-diacetyl-1,4-dihydrolutidine into the sorbent. Therefore, based on the obtained results, 0.03 g mL^{-1} NaCl was selected for further testing (Figure 7b).

3.3.4. The Time of Extraction

The extraction time in SPME is crucial as it influences the analytical response. Although the greatest sensitivity of SPME methods is observed when the extractions are performed at equilibrium, reaching this state may be very long. In the present experiment, the influence of time on the extraction was examined at 5, 10, 15, 20, 25, and 30 min. The results presented in Figure 7c show the optimal value at 20 min and no further increase of analytical signal was gained at 25 and 30 min.

3.3.5. The Time of Desorption

The desorption time is a meaningful factor in SPME. It should be long enough to desorb the analytes, but lengthening this time may unnecessarily worsen the analysis throughput. In the present study, the desorption was evaluated at 2, 4, 6, 8, 10, and 12 min, and the obtained results are presented in Figure 7d. Based on them, the optimum time of desorption was established at 8 min.

3.4. Analytical Performance

The method performance was verified to validate its use. The formaldehyde calibration curve was prepared at 7 levels of concentration (0.10, 0.25, 0.50, 1.0, 2.5, 5.0, 10 ng mL^{-1}) and correlation coefficient was equal to 0.9993. For calculating the limit of detection (LOD) a signal-to-noise ratio equal to 3 was used, and a value of 10 was selected for the limit of quantitation (LOQ). The LOD was 0.15 ng mL^{-1} and LOQ was 0.50 ng mL^{-1} . The recovery found in ultrapure water spiked at level 5.0 ng mL^{-1} was 86.1%. The enrichment factor that was calculated as the ratio of the peak area of formaldehyde with and without using the DES-TF-SPME method was equal to 178. Both single sorbent and sorbent-to-sorbent precision are satisfactory with the relative standard deviation values of 3.3% and 4.8%, respectively. This demonstrated that the newly prepared DES-3(1:3) sorbent is suitable for selective extraction of formaldehyde derivative and its stability on mesh support gives the possibility to use it at least 5 times after conditioning. Analytical figures of merit for the proposed DES-TF-SPME/HPLC-UV-Vis method are summarized in Table 2. A chromatogram of a formaldehyde derivative standard was visualized in Figure 8.

Table 2. The figures of merit obtained for the developed method.

Tested Parameters	Values
Linear range [ng mL^{-1}]	0.5–125
Regression equation	$y = 28.37x + 1.23$
Determination coefficient (r^2)	0.9995
Single sorbent RSD [%] ($n = 4$)	3.3
Sorbent-to-sorbent RSD [%] ($n = 4$)	4.8
Recovery [%]	86.1
Enrichment Factor	178
LOD [ng mL^{-1}]	0.15
LOQ [ng mL^{-1}]	0.50

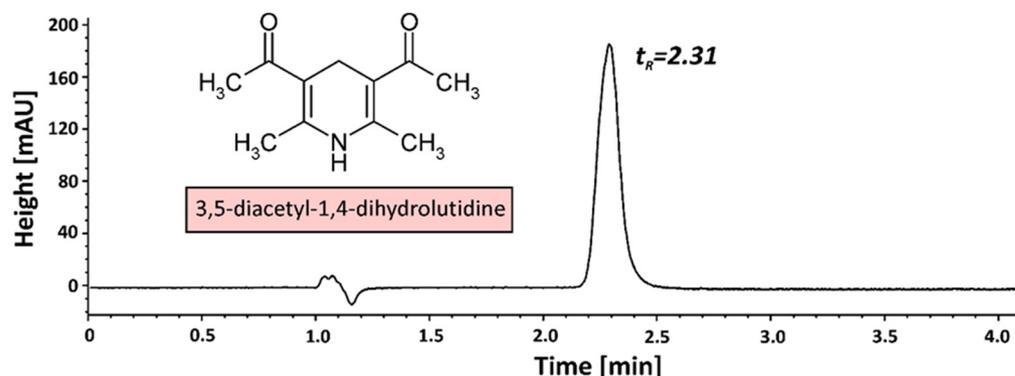


Figure 8. A chromatogram of a standard solution of formaldehyde derivative.

3.5. Application of the Method to Surface Water Samples

The developed method was tested on both river and lake water samples and its accuracy was evaluated. Spiking of formaldehyde was performed in four replicates at each of three concentrations, 0.5 ng mL^{-1} , 5.0 ng mL^{-1} and 10.0 ng mL^{-1} . The extraction efficiency of the method was calculated based on comparing the amount of formaldehyde extracted from the spiked samples with that determined in the non-spiked samples. However, as there was no formaldehyde detected in the lake and river water samples only the spiked amount was used for the calculation of recovery. A satisfactory recovery of formaldehyde from tested samples was shown (relative recovery from 78.0 to 99.1%). The repeatability for the medium and high levels was good (RSD in the range of 3.2–9.9%) but it was slightly worse for the low level—in the range of 14.6–18.8% (Table 3). Nevertheless, lower repeatability at the low level is acceptable because it is at the LOQ of the method. Thus, the developed method can be considered suitable for the determination of formaldehyde in surface waters.

Table 3. The results for the determination of formaldehyde in surface water samples.

Sample of Natural Water	Initial [ng mL^{-1}]	Spiked [ng mL^{-1}]	Measured [ng mL^{-1}]	RSD [%] ($n = 4$)	RR [%]
Malta Lake	nd	0.5	0.41 ± 0.06	14.6	82.0
		5.0	4.55 ± 0.19	4.2	91.0
		10.0	9.88 ± 0.45	4.6	98.8
Baba Lake	nd	0.5	0.39 ± 0.07	17.9	78.0
		5.0	4.58 ± 0.22	4.8	91.6
		10.0	9.74 ± 0.40	4.1	97.4
Kórnickie Lake	nd	0.5	0.48 ± 0.09	18.8	96.0
		5.0	4.34 ± 0.43	9.9	86.8
		10.0	9.91 ± 0.38	3.8	99.1
Cybina River	nd	0.5	0.43 ± 0.07	16.3	86.0
		5.0	4.45 ± 0.14	3.2	89.0
		10.0	9.67 ± 0.35	3.6	96.7
Warta River	nd	0.5	0.45 ± 0.08	17.8	90.0
		5.0	4.21 ± 0.17	4.0	84.2
		10.0	9.54 ± 0.31	3.3	95.4

nd—not detected; RR—relative recovery.

3.6. Reusability of the Sorbent

The reusability of the sorbent was studied on three independent sorbents. Each of the tested sorbents was used 5 times for extraction of water samples spiked at 50 ng mL^{-1} . The results given in Table 4 show the good stability of the DES sorbent and the possibility of its repeatable usage.

Table 4. Reusability of DES sorbents.

Extraction Cycle	Concentration [ng mL ⁻¹]		
	Sorbent 1	Sorbent 2	Sorbent 3
1	41.5	41.9	42.0
2	41.9	41.7	41.6
3	41.4	41.3	41.7
4	41.2	41.4	41.1
5	38.4	38.9	39.1
Average	40.9	41.0	41.1
RSD [%]	3.4	3.0	2.8

3.7. Comparison with Different Microextraction Methods Used for Determination of Formaldehyde in Real Samples

Formaldehyde, due to its toxic properties, is often analyzed in various samples (Table 5) [8–10,15–18,23]. Several sample preparation methods were used in these studies based mainly on SPME and DLLME. Nash reagent and 2,4-dinitrophenylhydrazine were two main derivatizing agents. Compared to these methods, the one proposed in the present study offers LOD similar to other methods based on HPLC-UV detection [7,8] as well as micro-spectrophotometric detection [17]. Much better LOD was obtained compared to spectrofluorimetric detection [18] and surprisingly to GC-MS detection [23]. Furthermore, the results obtained for the new DES-based sorbent show new possibilities offered by this new class of sorbents that due to the ease of their synthesis and modification of their properties enable synthesis directed to the intended purpose.

Table 5. Overview of the analytical performance of different microextraction methods for preconcentration of formaldehyde and comparison with the proposed method.

Microextraction Method	Detection Technique	Sorbent or Extractant	Derivatization Agent	Sample	LOD [ng mL ⁻¹]	RSD [%]	Refs.
SPME	GC-FID	PDMS/DVB	PFBHA	hair gel particle board indoor air	- *	- *	[15,16]
SPME	ID-MS	PDMS/DVB	PFPH	Cosmetic products	3.9	3.8–7.8	[23]
USAEME	micro-SP	CH ₂ Cl ₂	Nash reagent	Cosmetic products	0.02	5.9	[17]
IL-DLLME	HPLC-UV	[C ₈ MIM][PF ₆]	DNPH	room air, tap water, soils	0.01	1.3–6.8	[8]
LDM-DLLME	HPLC-UV	BA:MEOH	DNPH	tap water, juice, vaccine	0.05	3.0–8.0	[7]
RP-DLLME	HPLC-UV/Vis	H ₂ O	Nash reagent	Cosmetic products	0.7	1.9–9.2	[9]
DES-VA-LLME	HPLC-DAD	TAC:CP (1:1)	DNPH	indoor air	0.2 **	1.1–3.5	[10]
AA-DLLME-SPO	SF	thymol	Nash reagent	milk	15	<9.0	[18]
DES-TF-SPME	HPLC-UV/Vis	DES	Nash reagent	lake water river water	0.15	3.3–4.8	this work

* not given; ** µg mL⁻¹; SPME—solid phase microextraction; GC-FID—gas chromatography with flame ionization detector; MS—mass spectrometry; PDMS—poly(dimethylsiloxane); DVB—divinylbenzene; PFBHA—o-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride; PFPH—pentafluorophenylhydrazine; RP—reversed phase; USAEME—ultrasound-assisted emulsification microextraction; micro-SP—micro-spectrophotometry; IL—ionic liquid; DLLME—dispersive liquid-liquid microextraction; LDM—low density miniaturized; DES—deep eutectic solvent; VA—vortex assisted; LLME—liquid-liquid microextraction; TAC—trioctylmethylammonium chloride; CP—4-cyanophenol; DNPH—2,4-dinitrophenylhydrazine; AA—air assisted; BA—butyl acetate; SF—spectrofluorimetry; HPLC-UV/Vis—high performance liquid chromatography with ultraviolet/visible detection.

4. Conclusions

In this research, the synthesis of new DES sorbent materials and their coating on mesh support has been presented. The thin films formed from DES are promising sorbents for the preconcentration of formaldehyde from environmental water samples. The presented method was validated and found precise and repeatable. Also, thanks to a high enrichment factor capable of quantifying formaldehyde at trace concentration levels. Moreover, the synthesized DES belongs to a new class of sorbents that can be aimed at the preconcentration of selected analytes.

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