Application of Zn(II) Coordination Polymer with 1,3,5-Tris(4-carboxyphenyl)benzene as a Sorbent for Solid-Phase Extraction in the Determination of Polychlorinated Dibenzo-P-Dioxins, Dibenzofurans and Biphenyls by the Gas Chromatography/High-Resolution Mass Spectrometry

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The coordination polymer $\{[Zn_4O(BTB)_2]\cdot H_2O\}_n$ (H_3BTB – 1,3,5-tris(4-carboxyphenyl)benzene) was synthesized and tested as a solid-phase extraction sorbent for the determination of highly toxic organic pollutants: polychlorodibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), dioxin-like and non-dioxin-like polychlorinated biphenyls (PCBs) in natural water samples by the method of gas chromatography/high-resolution mass spectrometry (GC-HRMS). The results demonstrated that $[Zn_4O(BTB)_2]_n$ is an effective sorbent for solid-phase extraction of PCDD, PCDF, and PCBs from water samples with a mass fraction of suspended solids less than 1%. The effectiveness of the proposed combination of sample preparation and GC-HRMS analysis was studied for linearity, precision and reproducibility for 7 polychlorinated dibenzo-p-dioxins, 10 polychlorinated dibenzofurans, 12 dioxin-like and 6 non-dioxin-like polychlorinated biphenyls, the content of which is regulated by the European Union Directives. The limits of quantification (LOQ) for dioxins were found to be in the range of 2.5–18.8 pg L^{-1} and 3.2–14.0 pg L^{-1} for dioxins and dibenzofurans, respectively. Samples of natural surface waters were analyzed using both the developed SPE method and the liquid-liquid extraction method. All data obtained by the two research methods are in good agreement with each other.

Keywords: coordination polymer, zinc(II), 1,3,5-tris(4-carboxyphenyl)benzene, PCDD, PCDF, PCBs, GC–HRMS

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), dioxin-like and non-dioxin-like polychlorinated biphenyls (PCBs) are highly toxic organic pollutants. The content of dioxin-like contaminants is controlled in food and feed (EU Regulations 2017/644-771), as well as in the environment and industrial emissions (Directive 2008/105/EC, Directive 2010/75/EU, Regulation 2019/1021 and others). Gas chromatography combined with high-resolution mass spectrometry (GC-HRMS) is currently the most sensitive and reliable method for identifying these substances and verifying compliance with their maximum levels [1,2]. Given the low concentrations of these analytes in the samples, purification, fractionation, and concentration of the samples is a multi-stage process that requires expensive equipment, specialized sorbents, and large amounts of organic solvents. To reduce the consumption of organic solvents and the time costs of liquid-liquid extraction in the determination of PCDDs, PCDFs, and PCBs in water samples, solid-phase extraction (SPE) methods using SPE cartridges [3] or SPE membrane discs [4-7] are being intensively developed. The ability of modified sorbents or membranes with grafted octadecyl (C_{18}) groups to sorb non-polar compounds from aqueous solutions is the basis of such methods. The nonselective sorption of PCDDs, PCDFs, and PCBs on C18-modified materials is a disadvantage of solid-phase extraction, as the parallel sorption of other non-polar compounds leads to interferences with matrix components, reducing the extraction coefficients and the sensitivity of the analysis.

Currently, hybrid organic-inorganic materials composed of aromatic ligands and d-metals are being investigated as sorbents for solid-phase extraction of polycyclic aromatic hydrocarbons, PCDD, PCDF, and PCBs at low concentrations from environmental samples [8,9]. Such sorbents are thermally and chemically stable, have a large pore volume and extended surface area, and exhibit high selectivity due to adsorption mechanisms based on hydrophobic effects, dipole-dipole interactions, and π-π stacking [10]. In addition, applying metal-organic framework

structures to SPE sorbents is an environmentally friendly approach, as they can be recycled and allow a significant reduction in organic solvents compared to liquid-liquid extraction.

Metal-organic framework structures of Zn(II) with polyaromatic ligands [11-16] are of interest in this regard, in particular coordination polymers of Zn(II) with 1,3,5-tris(4-carboxyphenyl)benzene (H_3BTB) with a meso- (pore size 2–50 nm) or microporous (pore size < 2 nm) structure [12-15]. The composition and structure of these complexes depend on the synthesis conditions and starting reagents, for example, $[Zn_4O(BDC)(BTB)_{4/3}]$ (H_2BDC – terephthalic acid) [15], $[Zn_4O(NDC{-}OH)(BTB)_{4/3}]$ ($H_2(NDC{-}OH)$ – 4,8-dihydroxynaphthalene-2,6-dicarboxylic acid) [13], $[Zn_4O(BTB)_2]\cdot H_2O$, $[Zn_4O(BTB)_2]\cdot DMF\cdot H_2O$, $[Zn_6O(BTB)_4]\cdot 2(H^+)\cdot 2DMF\cdot 4H_2O$ (DMF – dimethylformamide) [12].

In this work, we investigated the monoligand coordination polymer of Zn(II) with 1,3,5-tris(4-carboxyphenyl)benzene (H_3BTB) as a SPE sorbent for the determination of PCDD, PCDF, dioxin-like, and non-dioxin-like PCBs. Since, as previously shown [17], this coordination polymer, impregnated on stainless steel fibers, is an effective sorbent for the chromatographic-mass spectrometric determination of some polychlorinated biphenyls (PCB 01, 05, 29, 47, 98, 154, 171, 201) and several polycyclic aromatic hydrocarbons (naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene) in water samples by solid-phase microextraction (SPME-GC-MS).

Experimental part

Reagents and materials. Reagents for the synthesis were purchased from Sigma-Aldrich® and used without further purification: 1,3,5-tris(4-carboxyphenyl)benzene (H_3BTB, $C_{27}H_{18}O_6$, CAS 50446-44-1, ≥98%), $Zn(NO_3)_2\cdot 6H_2O$ (CAS 10196-18-6, ≥99%), dimethylformamide (DMF, $HCON(CH_3)_2$, CAS 68-12-2, ≥99%). Toluene, dichloromethane, nonane, acetone, methanol of “HPLC grade” qualification, and hexane of “Pesticide Residue Analysis” (≥95%, CHROMASOLV™) qualification were used in the work. All reagents used to determine PCDD, PCDF, and PCBs were checked for the absence of contamination through a “blank experiment”.

Non-labelled PCDD, PCDF, and PCBs and Carbon-13 (^{13}C) isotope-labelled PCDD-$^{13}C_{12}$, PCDF-$^{13}C_{12}$, and PCB-$^{3}C_{12}$ standards, with a content error for each congener of no more than ± 5%, were obtained from Wellington Laboratories (Ontario, Canada).

The following analytes were studied in the work:

PCDDs: tetrachlorodibenzo-*p*-dioxin 2378-TCDD, pentachlorodibenzo-*p*-dioxin 12378-PeCDD, hexachlorodibenzo-*p*-dioxins 123478-HxCDD, 123678-HxCDD and 123789-HxCDD, heptachlorodibenzo-*p*-dioxin 1234678-HpCDD, octachlorodibenzo-*p*-dioxin OCDD;

PCDFs: tetrachlorodibenzofuran 2378-TCDF, pentachlorodibenzofurans 12378-PeCDF i 23478-PeCDF, hexachlorodibenzofurans 123478-HxCDF, 123678-HxCDF, 234678-HxCDF and 123789-HxCDF, heptachlorodibenzofurans 1234678-HpCDF and 1234789-HpCDF, octachlorodibenzofurans OCDF;

PCBs: dioxin-like polychlorinated biphenyls PCB77, PCB81, PCB126, PCB169, PCB105, PCB114, PCB118, PCB123, PCB156, PCB157, PCB167, PCB189 and non-dioxin-like (indicator) PCB28, PCB52, PCB101, PCB138, PCB153, PCB180.

Apparatus. Powder X-ray diffraction patterns were recorded on an automatic diffractometer STOE STADI P (CuKα1 radiation). Energy-dispersive X-ray spectroscopy (TESCAN VEGA3 LMU electron microscope with Oxford Instruments Aztec ONE elemental microanalyser with X-Max^{N}20 drift Si-semiconductor detector) was used to determine the chemical composition of the compound (molar ratio of Zn/O components). Before the electron microscopy study, the synthesized material was deposited as a thin layer on a conductive, graphitized film and purged with an inert gas. SEM-images and energy-dispersive X-ray analysis results were obtained at 21-25 kV voltage and high vacuum atmosphere (9.0×10^{-3} Pa). The working distance was 15-18 mm, and the electron beam intensity was reduced to 70% due to the low electrical conductivity of the sample.

The hydrate composition and the character of thermal decomposition were determined by thermogravimetry (derivatograph of the Paulik-Paulik-Erdey system Q-1500 D, sample heating rate – 10 degrees/min, standard – calcined alumina, platinum crucible, static air atmosphere, temperature range 20-1000°C). The carbon and hydrogen content in the complex composition was determined using the Elemental Analyzer CE-440 C, N, H analyzer (sample mass: ~2 mg in tin capsules; analysis time: 5 min; 110/220 V, 60/50 Hz, 10 A). Zinc content was determined with an optical emission spectrometer with inductively coupled plasma, Optima 8000 PerkinElmer (Rf power 1300W, plasma viewing: axial, plasma argon flow rate 8 L min^{-1}, nebulizer argon flow rate 0.7 L min^{-1}, auxiliary argon flow rate 0.2 L min^{-1}, sample uptake rate 1.5 mL min^{-1}). The nebulization system was equipped with a chemical-resistant concentric glass nebulizer (Meinhard type) coupled to a glass cyclonic spray chamber. A torch with an alumina injector was used. A microwave accelerated reaction digestion system (MARS, SEM Corporation, USA) was employed to perform the acid digestion of 0.5 g of sorbent samples with 4 mL of HNO_3 (65% v/v) and 2 mL of H_2O_2 (30% v/v). The IR spectra in the range of 4000-400 cm^{-1} were recorded as potassium bromide pellets on a Frontier spectrometer (PerkinElmer).

Chromatography, coupled with high-resolution mass spectrometry (GC-HRMS), was used to measure dioxin-like compounds, with a chromatographic

system consisting of a TRACE™ 1310 GC gas chromatograph (Thermo Fisher Scientific, USA) and a DFS™ Magnetic Sector GC-HRMS System (Thermo Fisher Scientific, USA). GC-HRMS was equipped with a 60 m capillary column (0.25 mm ID) with a special stationary phase (0.20 μm thickness), which allows chromatographic separation of hexasubstituted dioxin and furan isomers. Mass spectrometric measurements were performed in the selected ion monitoring (SIM) mode using perfluorotributylamine (FC-43) as a mass calibration standard. The identification and determination of PCDD/DF and PCBs were performed by comparing the retention times and the signal ratios of the two selected ions with those of internal isotope-labelled standards.

Synthesis. The Zn(II) coordination polymer with H_3BTB was prepared according to the method reported in [12], with some modifications. A portion of H_3BTB (0.4495 g, 1.025 mmoL), $Zn(NO_3)_2 \cdot 6H_2O$ (0.5735 g, 1.928 mmoL), and 50 mL of DMF were mixed in a beaker. The beaker was placed in an ultrasonic bath and kept under ultrasound for 15 minutes to obtain a homogeneous solution. The beaker contents were transferred to five 20 mL glass vials with an 18 mm headspace thread, and each was filled halfway with the reaction mixture. The vials were closed with screw metal caps with PTFE/silicone septa, placed in a drying oven, and kept at 100°C for 24 h. After the specified time, the reaction mixture was slowly cooled to room temperature. The supernatant was decanted and replaced with acetone (10 mL). The acetone was decanted and added three times again over three days. The resulting precipitate was dried at 60°C for 3 hours. The yield of the resulting product was 42% based on H_3BTB. Found, %: C – 55.49, H – 2.69, Zn – 22.38; calculated for $C_{54}H_{32}O_{14}Zn_4$, %: C – 55.57, H – 2.74, Zn – 22.47.

Method for the determination of PCDD, PCDF, dioxin-like and non-dioxin-like PCBs in water samples using SPE concentration. The work used deionized water as a blank, deionized water spiked with standard solutions of PCDD/DF and PCBs, and natural water samples with a mass fraction of suspended solids less than 1%, collected at water intake points from the Dniester River in the Odessa region. Natural water samples were stored in amber glass containers at 4°C until analyzed. The sorbent (150.0±0.1 mg) was tightly pressed into a polypropylene cartridge between two PTFE frits. The cartridge prepared in this way was placed in a vacuum manifold. A solution of $^{13}C_{12}$-labeled internal standards in tetrahydrofuran was added to the water sample (500.0±0.1 L), mixed on a shaker for 1 h to establish equilibrium, and passed through the cartridge under vacuum at a rate of 1 drop per 2-3 seconds. The cartridge was then dried under vacuum. The cartridge was eluted with 6 mL of acetone to remove traces of water, followed by 15 mL of toluene for analyte desorption at a flow rate of 1 drop every 3-5 seconds. According to research [18], toluene is the most effective solvent for eluting organic aromatic pollutants due to π- π interactions. The resulting solution was passed through a paper filter with a layer of sodium sulfate. For natural water samples, the cartridge was washed with 2 x 4 mL portions of deionized water before elution with organic solvents. The solvent volume was reduced to a few milliliters, transferred to a vial, and evaporated under a gentle stream of nitrogen. Then, the recovery standards solution in isooctane (20 μL) was added. PCDDs and PCDFs (17 contaminants), dioxin-like PCBs (12 analytes), and non-dioxin-like PCBs (6 compounds) were analyzed by isotope-dilution gas chromatography coupled to high-resolution mass spectrometry.

The SPE procedure was developed using water samples spiked with PCBs at ng L^{-1} and dioxin-like compounds at pg L^{-1}. The matrix effect was also assessed by studying real water matrices. Recovery for spiked samples was calculated as the ratio of the measured concentrations to the theoretical concentration in three replicate experiments (n = 3). Validation criteria of the optimized method, such as linearity, sensitivity, and precision, as well as the limits of detection (LOD, S/N > 3) and quantification (LOQ, S/N > 10) for each congener, were evaluated. The isotope dilution method was used for quantification. Surface water samples were analyzed by two methods: TFE and liquid-liquid extraction using dichloromethane as the organic extractant. To discuss the toxicity of the samples, results were expressed as both concentrations (pg L^{-1}) and WHO pg-TEQ/L.

Results and discussion

Previous research [12] has found the influence of crystallization conditions (solvent, time, temperature) on the phase composition of the Zn(II) coordination polymer obtained with H_3BTB. In the DMF environment, solvent molecules act as templates. The denser ordered phase is formed at a temperature of 100°C, which can be reduced to a periodic arrangement of octahedral vertices of the basic zinc carboxylate $[Zn_4O(CO_2)_6]$, united by three-top planar linkers BTB^{3-}. In appearance, the obtained coordination polymer is a soldered rod-shaped crystal, ranging from colorless to white.

The molar ratio of elements in the compound according to the results of elemental analysis is Zn : C = 1 : 13.5. Therefore, the composition Zn : BTB = 2 : 1 is realized, which corresponds to the coordination site $[Zn_4O(CO_2)_6]$.

The powder XRD pattern (Fig. 1) indicates the material is X-ray amorphous. One clear, intense peak at 2θ ~5.46° demonstrates an ordered structure with a distance between the crystalline layers of 15.929 Å. This diffraction pattern is typical of metal-organic framework structures with a homogeneous porous structure [19].

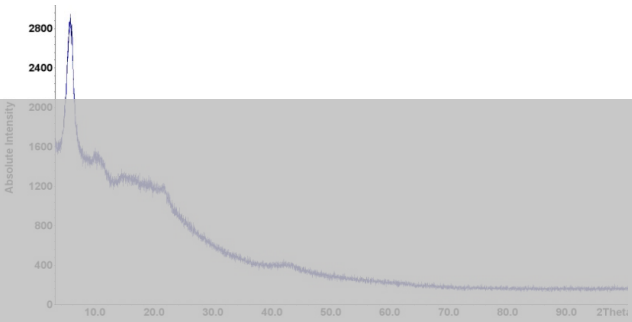

Fig. 1. Powder X-ray diffraction pattern of the synthesized complex.

According to the results of thermogravimetric analysis (TGA) of the prepared sample, the compound is a crystal hydrate (Fig. 2). The first endothermic effect in the temperature range of 80-200°C is a result that one molecule of crystallization water is eliminated into the gas phase (Dm_{TG}=1.50%, Dm_{theor}=1.54%) without further weight loss up to 400°C. The second weight loss at >400°C corresponds to the decomposition of the Zn-MOF spatial lattice with further decomposition of organic ligands from 450 to 720°C, resulting in the formation of an inorganic residue. The final product of thermal decomposition at >750°C is zinc oxide (Dm_{TG}=72.50%, Dm_{theor}=72.04%). The obtained data indicate that the framework structure is thermally stable up to ~400 °C. Thus, this material can be regenerated by removing water and organic solvents from the pores when heated to 200 °C.

In the IR spectrum of the complex, vibrational bands (Fig. 3) characterize bonds in the coordination polyhedron of zinc. The bands n_{as}(C-O) = 1607 cm^{-1} and n_s(C-O) = 1407 cm^{-1}, characteristic of carboxylate anions, and there is no band of protonated carboxyl group in the region of 1725 cm^{-1}, clearly indicate that carboxylate groups of the ligand are bound to zinc in the molecule. That confirmed the presence of the band for the stretching vibration of the Zn-O bond at 482 cm^{-1} [20].

As can be seen from the scanning electron microscopy (SEM) images (Fig. 4a), the obtained material is agglomerates of nanosheets with a complex system of branched internal cavities and randomly formed surface defects, which form the inner surface of the porous material from the walls of all cracks, pores, and cavities. Thus, the SEM image demonstrates the highly porous morphology of the obtained coordination polymer.

The element ratio Zn : O = 1 : 3.4, established by energy dispersive X-ray spectroscopy, confirms the composition of the complex (Fig. 4c). The distribution of elements (Fig. 4b) proves the homogeneity of the sample, uniform pore distribution, and the potential for its use as a sorbent.

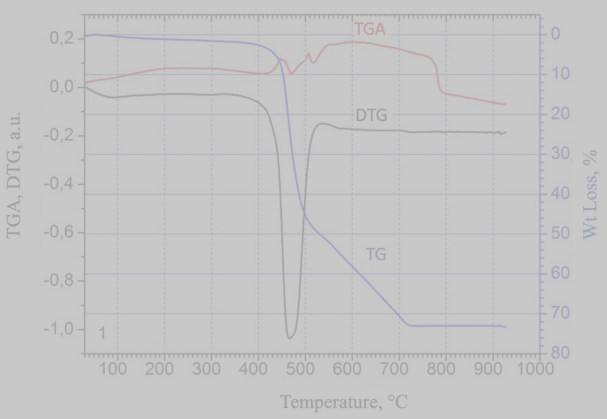

Fig. 2. Thermogravimetric analysis (TGA) of the prepared sample.

The obtained data on the physicochemical characteristics of the synthesized complex, and their comparison with those reported in [12], confirm its polymeric structure and the possibility of further use in the determination of dioxins and dioxin-like compounds.

It is known that separating PCBs and PCDD/Fs, as well as analytes and matrix-interfering compounds, is an important challenge in developing gas chromatographic methods for their determination [21,22]. The optimized conditions that allow for effective separation and determination of target compounds are given in Table 1.

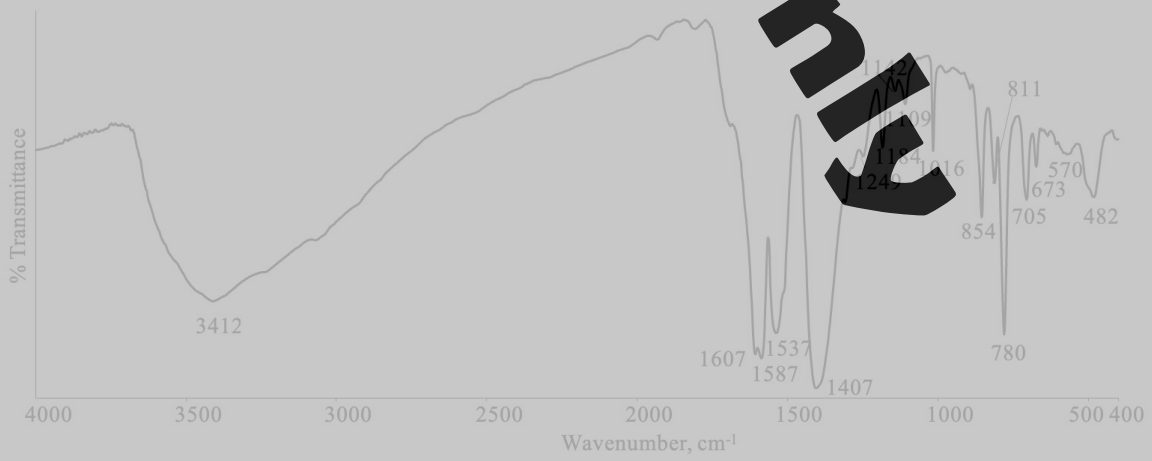

Fig. 3. IR spectra of the complex.

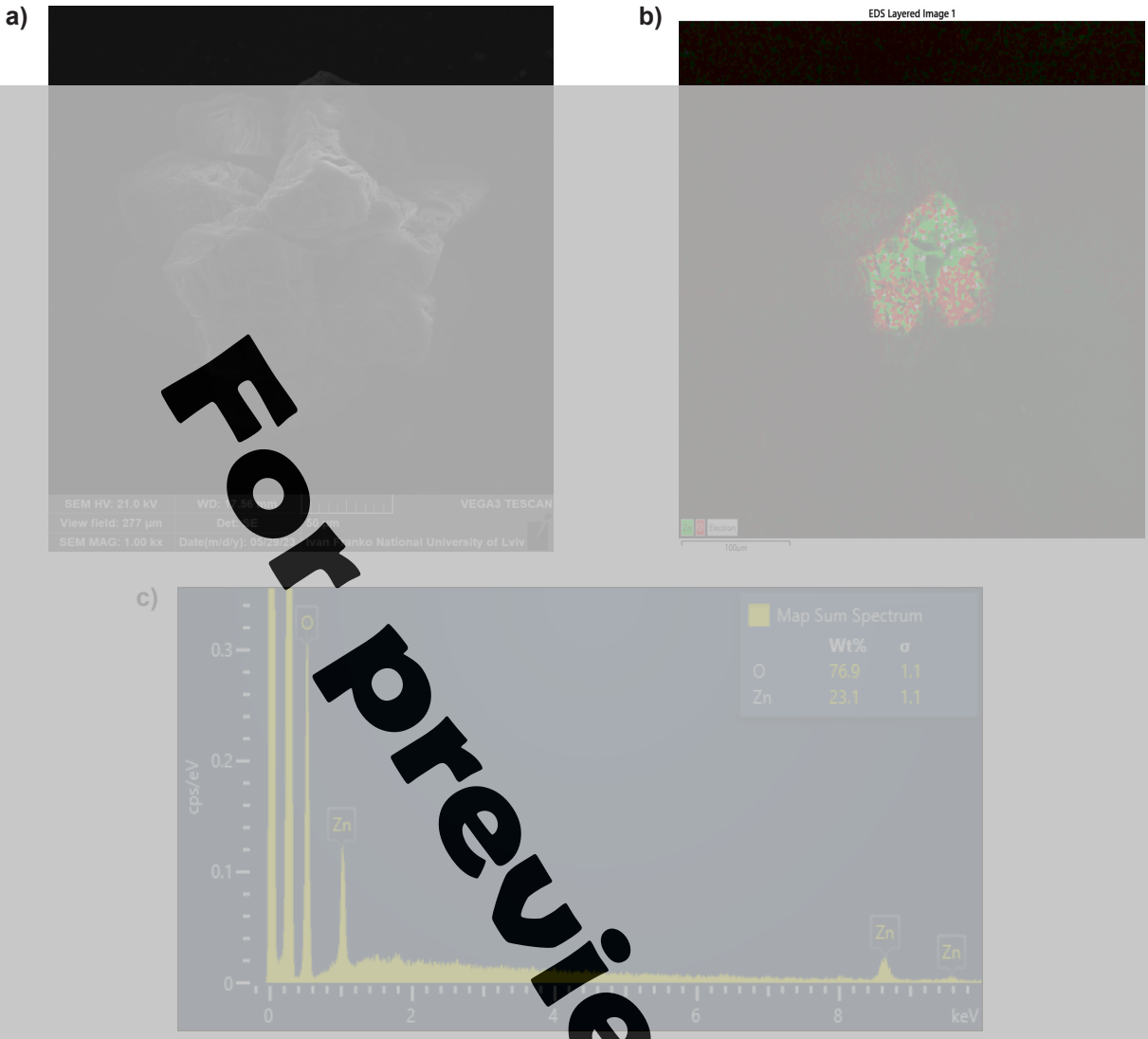

Fig. 4. a – SEM image of the synthesized complex at a magnification of 1000 times; b – elemental distribution on the grain surface; c – energy-dispersive X-ray spectrum of the synthesized sorbent.

Table 1. Method parameters used for GC-HRMS.

	Parameter	Method for PCDD/F	Method for PCB
GC	Injection mode	Splitless	Splitless
	Injector temperature	280°C	280°C
	Carrier gas	Helium, 0.8 mL/min	Helium, 0.8 mL/min
	Column	Zebron ZB-Dioxin 60m×0.25mm, 0.2 μm	
	Oven program	180°C (2 min)-8°C/min,240°C (0 min)-2°C/min,320°C (8 min)	160°C (2 min)-6°C/min,240°C (8 min)-6°C/min,320°C (8 min)
MS	Ionization mode	Electron impact (EI)	
	Detection mode	Selected ion monitoring (SIM)	
	Ionizing current	0.6 mA	
	Electron impact energy	45 eV	
	Resolution	> 10 000 (10% height)	

To separate the positional isomers of PCBs and PCDD/Fs, a 60 m capillary column with a 0.25 mm inner diameter and a special stationary phase with a 0.25 μm film thickness was used. The obtained chromatograms are shown in Fig. 5. High-resolution mass spectrometric measurements were performed at a resolution of R > 10,000 at 10% of the peak height, which allows selective detection of analytes and reduces background intensity.

The method's validation characteristics were assessed by extracting a series of deionized water samples spiked with standard solutions containing all analytes of interest. The limits of quantification (LOQ) for dioxins were found to be in the range of 2.5–18.8 pg L^{-1} and 3.2–14.0 pg L^{-1} for dioxins and dibenzofurans, respectively (Table 2). The higher values observed for octa-substituted compounds are associated with both lower recovery coefficients than those of congeners with fewer chlorine atoms and lower equipment sensitivity for octa-derivatives. For comparison, the limits of quantification of dioxins and dibenzofurans by the liquid-liquid extraction (LLE) method are 12.5-78.5 pg L^{-1} from tetra- to octa-substituted compounds. At the same time, the liquid extraction method uses a sample volume twice as large. Thus, the SPE method is more sensitive than the LLE. The linearity of the method for PCDD/DF was investigated in the range of 5 to 4000 pg L^{-1}. The obtained data regarding the linearity range are given in Table 2. The correlation coefficients (r) ranged from 0.993 to 0.999. Repeatability values obtained from six replicate tests of a water sample spiked with 500 pg L^{-1} PCDD/DF ranged from 2.2% to 9.7% and from 2.7% to 10.8% for dibenzodioxins and dibenzofurans, respectively.

The limit of quantification (LOQ) is in the range of 3.1-8.1 pg L^{-1} and 4.9-7.5 pg L^{-1} for dioxin-like and non-dioxin-like PCBs (Table 3), respectively. The LOQs of PCBs obtained by the LLE method are 15.0-32.8 pg L^{-1}. The linearity of the method for PCBs was investigated in the range from 5 to 5000 ng L^{-1}. The obtained calibration curves were characterized by correlation coefficients (r) ranging from 0.994 to 0.997. The repeatability values obtained from six repeated tests of a water sample spiked with 100 pg L^{-1} PCBs ranged from 5.6% to 11.8%.

Samples of natural surface waters were analyzed using both the developed SPE method and the liquid-liquid extraction (LLE) method. In both cases, the isotope dilution method was used for the calculations, with a standard solution of $^{13}C_{12}$-labeled analytes added to the samples before testing. This approach eliminates analyte losses and matrix effects, since the physicochemical properties of the analytes and the internal standards are identical. The test results are summarized in Table 4.

The results showed insignificant contamination of samples 1 and 3 with octadioxins. 1234678-HpCDF and OCDF were also detected in sample 3. Dioxin-like PCB77, PCB105, and PCB118, the most common among this class of contaminants, were detected in the studied samples, which, according to literature data [23], indicates an insignificant degree of contamination, primarily associated with the burning of wood and coal. The total concentrations of PCDD/DF and dioxin-like PCBs, expressed in WHO-TEQ 2005 units, were 0.009, 0.001, and 0.105 pg-TEQ WHO/l for samples 1, 2, and 3, respectively. All data obtained using the two research methods are in good agreement.

Table 2. Analytical performance of the method for dioxins and dibenzofurans compounds.

Congener	Limit of quantification LOQ (pg L^{-1})	Linear range (pg L^{-1})	Repeatability (RSD, n = 6, 500 pg L^{-1}) (%)	Recovery $R_{average}$ (%)
2378-TCDD	2.5	5-4000	2.2	72.1±2.3
12378-PeCDD	3.7	5-4000	3.1	68.8±0.5
123478-HxCDD	5.0	5-4000	4.4	70.1±1.2
123678-HxCDD	4.6	5-4000	5.8	65.5±3.1
123789-HxCDD	3.5	5-4000	4.2	69.5±0.8
1234678-HpCDD	3.3	5-4000	3.7	71.5±2.5
OCDD	18.8	20-4000	6.7	61.5±1.3
2378-TCDF	3.2	5-4000	2.7	84.9±1.2
12378-PeCDF	4.0	5-4000	2.9	72.4±0.6
23478-PeCDF	4.2	5-4000	5.5	73.5±2.4
123478-HxCDF	7.2	10-4000	6.0	68.9±3.3
123678-HxCDF	8.0	10-4000	5.8	65.7±0.7
234678-HxCDF	5.4	10-4000	5.4	70.8±1.5
123789-HxCDF	5.5	10-4000	5.7	80.5±2.0
1234678-HpCDF	6.5	10-4000	6.1	82.4±1.3
1234789-HpCDF	6.8	10-4000	6.3	78.4±1.8
OCDF	14.0	20-4000	10.8	61.0±1.6

Fig. 5. Chromatographic separation of the most toxic PCDD/Fs congeners (1 ng mL^{-1} for octasubstituted compounds and 0.5 ng mL^{-1} for others): a – peak identification: (1) 2,3,7,8-TCDD; (2) 1,2,3,7,8-PeCDD; (3) 123478-HxCDD; (4) 123678-HxCDD; (5) 123789-HxCDD; (6) 1,2,3,4,6,7,8-HpCDD; (7) OCDD; b – peak identification: (8) 1368-TCDF (Recovery standard); (9) 2,3,7,8-TCDF; (10) 12378-PeCDF; (11) 23478-PeCDF; (12) 123478-HxCDF; (13) 123678-HxCDF; (14) 234678-HxCDF; (15) 123789-HxCDF; (16) 1234678-HpCDF; (17) 1234689-HpCDF (Recovery standard); (18) 1234789-HpCDF; (19) OCDF.

Table 3. Analytical characteristics of the method for PCBs.

Congener	Limit of quantification LOQ (pg L^{-1})	Linear range (pg L^{-1})	Repeatability (RSD, n = 6, 100 pg L^{-1}) (%)	Recovery $R_{average}$ (%)
		Dioxin-like PCBs		
PCB77	3.8	5-5000	8.3	74.2±3.1
PCB81	6.9	10-5000	5.6	81.1±2.4
PCB126	5.7	10-5000	7.2	62.5±0.8
PCB169	3.3	5-5000	6.4	72.0±1.7
PCB105	3.1	5-5000	5.8	82.7±1.2
PCB114	6.1	10-5000	8.2	61.6±2.6
PCB118	3.6	5-5000	7.2	74.0±1.4
PCB123	3.4	5-5000	9.4	69.1±0.9
PCB156	6.1	10-5000	8.6	62.5±2.3
PCB157	7.0	10-5000	7.9	66.2±1.7
PCB167	8.1	10-5000	7.3	64.8±0.8
PCB189	7.6	10-5000	8.6	61.8±1.4
		Non-dioxin-like (indicator) PCBs		
PCB28	4.9	10-5000	7.5	64.1±0.9
PCB52	7.5	10-5000	8.1	64.5±1.7
PCB101	5.2	10-5000	9.0	57.8±2.0
PCB138	7.2	10-5000	8.7	53.8±2.6
PCB153	7.5	10-5000	11.8	59.6±1.6
PCB180	5.0	10-5000	9.4	54.4±2.4

Table 4. Determination of dioxins and dioxin-like compounds in natural surface water samples.

Congener	Sample 1		Sample 2		Sample 3		Sample 1 spiked 100 pg L^{-1}	
	LLE	SPE	LLE	SPE	LLE	SPE	LLE	SPE
2378-TCDD	ND*	ND	ND	ND	ND	ND	98.8±2.7	97.1±1.8
12378-PeCDD	ND	ND	ND	ND	ND	ND	101.1±3.0	102.3±3.9
123478-HxCDD	ND	ND	ND	ND	ND	ND	97.2±3.1	101.0±2.6
123678-HxCDD	ND	ND	ND	ND	ND	ND	98.7±1.9	101.2±2.2
123789-HxCDD	ND	ND	ND	ND	ND	ND	101.5±1.4	104.4±1.9
1234678-HpCDD	ND	ND	ND	ND	ND	ND	98.7±1.7	99.6±2.0
OCDD	26.4 ±1.7	28.0 ±2.4	ND	ND	37.5 ±2.0	38.4 ±2.6	128.9±5.1	131.8±4.7
2378-TCDF	ND	ND	ND	ND	ND	ND	101.0±3.3	99.3±2.7
12378-PeCDF	ND	ND	ND	ND	ND	ND	98.6±4.7	100.3±5.0
23478-PeCDF	ND	ND	ND	ND	ND	ND	100.9±6.2	98.8±4.9
123478-HxCDF	ND	ND	ND	ND	ND	ND	98.7±3.4	99.7±2.9
123678-HxCDF	ND	ND	ND	ND	ND	ND	100.8±4.1	98.1±1.9
234678-HxCDF	ND	ND	ND	ND	ND	ND	102.2±3.6	101.9±2.1
123789-HxCDF	ND	ND	ND	ND	ND	ND	102.4±3.5	99.8±2.9
1234678-HpCDF	ND	ND	ND	ND	8.6 ±1.8	8.1 ±2.8	100.4±2.9	99.8±2.2
1234789-HpCDF	ND	ND	ND	ND	ND	ND	101.9±3.0	102.9±2.6
OCDF	ND	ND	ND	ND	20.7 ±1.3	19.4 ±2.1	100.6±6.3	99.1±5.1

Table 4. (continuation).

Congener	Sample 1		Sample 2		Sample 3		Sample 1 spiked 100 pg L^{-1}	
	LLE	SPE	LLE	SPE	LLE	SPE	LLE	SPE
PCB77	6.7 ±0.6	5.9 ±0.4	5.3 ±0.6	4.7 ±0.5	7.9 ±1.4	7.3 ±0.9	107.5±2.4	108.3±1.8
PCB81	ND	ND	ND	ND	ND	ND	99.7±1.2	98.1±1.4
PCB126	ND	ND	ND	ND	ND	ND	98.3±0.9	96.6±2.3
PCB169	ND	ND	ND	ND	ND	ND	99.4±3.5	101.1±3.3
PCB105	9.7 ±1.8	9.4 ±1.3	8.4 ±1.5	7.7 ±2.1	12.6 ±2.4	13.2 ±1.9	111.2±2.5	113.3±3.8
PCB114	ND	ND	ND	ND	ND	ND	98.4±4.2	102.1±3.7
PCB118	22.8 ±1.5	23.4 ±3.6	19.1 ±2.4	18.5 ±4.7	32.4 ±4.1	31.2 ±3.6	124.4±4.8	127.0±5.1
PCB123	ND	ND	ND	ND	ND	ND	101.6±6.1	97.3±5.7
PCB156	ND	ND	ND	ND	ND	ND	100.8±3.7	98.4±3.1
PCB157	ND	ND	ND	ND	ND	ND	99.1±4.0	101.7±4.2
PCB167	ND	ND	ND	ND	ND	ND	97.7±3.7	101.3±2.8
PCB189	ND	ND	ND	ND	ND	ND	98.3±4.8	97.5±3.5
Total content PCDD/DFs and PCBs, pg L^{-1}	65.6 ±8.3	66.7 ±9.5	32.8 ±6.4	30.9 ±5.2	119.70 ±12.5	118.1 ±9.7	2968.8±23.1	2979.8±34.3

* ND – not found (less than detection limit)

Conclusions

A monoligand coordination polymer of Zn(II) with 1,3,5-tris(4-carboxyphenyl)benzene was synthesized and characterized by elemental analysis, energy-dispersive X-ray spectroscopy, and thermogravimetry, confirming its polymeric structure. The possibility of its use as a SPE sorbent for the determination of PCDDs, PCDFs, dioxin-like and non-dioxin-like PCBs was investigated. The developed method was used to determine dioxins and dioxin-like compounds in local natural surface water samples. The advantages of the proposed SPE method compared to the traditional liquid-liquid extraction method are the absence of toxic organic solvents for extraction, a decrease in the volume of water sample for analysis due to concentration on the cartridges, a reduction in labor costs, and the possibility of automating the sample preparation process using the SPE procedure.

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