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Development and validation of a gas chromatography method for analysing polychlorinated biphenyls in fish roe

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ABSTRACT

A method for determining polychlorinated biphenyls (PCBs) in fish roe by gas chromatography (GC) has been developed. The suitability (validation) of the process for the determination of 14 PCBs (PCB 18, PCB 31, PCB 28, PCB 52, PCB 44, PCB 101, PCB 149, PCB 118, PCB 153, PCB 138, PCB 180, PCB 170, PCB 194, PCB 209) in fish roe by GC using an electron capture detector (ECD) was evaluated according to the following criteria: selectivity, linearity, limits of detection (LOD), limits of quantification (LOQ), accuracy and precision. Automated Soxhlet extraction and sample clean-up by solid phase extraction (SPE) were proposed for extracting PCBs from fish roe. The results of the method selectivity study showed that the determination of PCBs in fish roe is not affected by other components in the sample. The correlation coefficients for fourteen PCBs ranged from 0.9962 to 0.9999 (R^2 ≥0.995). The limits of detection (LOD) and limits of quantification (LOQ) of PCBs are below the maximum permissible levels set by the European Union (EU). The recovery percentage ranged from 81.5% to 107%, indicating the PCB extraction procedure's acceptability (R, 80 – 120%). The relative standard deviation (RSD, %) of the measurement results under convergence conditions ranged from 1.02% to 9.43% (RSD ≥15%). The obtained method suitability (validation) data meets the Commission Regulation (EU) No 589/2014 criteria.

Keywords: fish roe, polychlorinated biphenyls, PCB, gas chromatography, GC, method validation

INTRODUCTION

The world produces record quantities of fisheries and aquaculture products **[1]**. According to the European Commission, the average consumption of fish and fish products in the European Union (EU) has increased to 24.4 kg per person per year **[2]**. Global production of fish and fish products is forecast to increase by 14% by 2030. The largest importers of salmon roe in the EU are France, Germany, and Sweden, which account for 57% of total imports. In Asia are Japan, South Korea and Thailand, with a combined share of 77% of total imports. The leading suppliers of roe to the US are Taiwan, Japan and Iceland, with a combined share of 68% of total imports **[3]**.

Due to objective circumstances, Ukraine cannot catch or grow a significant amount of fish and seafood, so more than 85% of all fish products, including roe, are imported by Ukrainians. The largest quantities of fish and fish products have been imported into Ukraine from Norway, Iceland, the USA, Canada, Estonia and other countries **[4]**.

Fish roe is a particularly valuable food product, containing many nutrients **[5]**. For example, consuming 25 grams of fish roe can provide half of the body's daily protein requirement. Fish roe is also beneficial due to its micro- and macronutrients, including vitamins A, B12, B6, and D **[6]**, **[7]**.

Compared to other foods such as meat **[8]**, **[9]** and eggs **[10]**, marine fish roe contains a high amount of omega-3 fatty acids. The main fatty acids in roe are palmitic (C16:0), oleic (C18:1ω-9), linoleic (C18:2ω-6), cis-4,7,10,13,16,19-docosahexaenoic (C22:6ω-3), cis-5,8,11,14,17-eicosapentaenoic (20:5ω-3) and cis-11,14,17-eicosatrienoic (C20:3n3) acids **[11]**, **[12]**, **[13]**.

Considering the increase in the volume of fish products sold to the public **[14]**, it is necessary to strictly control the maximum permissible levels of contaminants by the current regulations in Ukraine and the world **[15]**. Among the indicators of fish roe safety, an important place is occupied by the determination of such toxic xenobiotics as polychlorinated biphenyls (PCBs). To date, 209 individual PCB congeners are known, which can accumulate in fats due to their lipophilic properties **[16]**, **[17]**. The high toxicity of these substances and their harmfulness to living organisms has been demonstrated by many scientists **[18]**, **[19]**, **[20]**, **[21]**.

According to the State Sanitary Rules and Regulations **[22]** and the requirements of the EU Directive **[23]**, the total amount of six PCBs (PCB 28, PCB 52, PCB 101, PCB 138, PCB 153 and PCB 180) in fish products should not exceed 75 ng/g (0.075 mg/kg). These regulations do not consider the contamination of eggs by other PCBs that may be present in fish products. Studies have also shown that the accumulation of PCBs in fish varies depending on the part of the fish analysed and that the sampling method may affect the result **[24]**.

Gas chromatography with mass spectrometric detection (GC/MS) **[25]** and gas chromatography with electron capture detection (GC/ECD) **[26]** are used to quantify PCBs.

Sample preparation by modern GC/ECD methods for determining PCBs in fat-containing objects is based on solvent extraction of the samples, purification with 90% sulfuric acid, centrifugation, and evaporation to dryness in a stream of nitrogen, followed by the addition of a solvent and purification on SPE columns **[27]**. The relevant normative documents specify the methods for determining PCBs in high-fat food products **[28]**, **[29]**, **[30]**, including fish roe, require complex and time-consuming sample preparation, i.e. they are rather labour-intensive and multi-step **[31]**, **[32]**, **[33]**. Therefore, it is important to improve the existing methods and develop new ones for the quantitative determination of PCBs in fish roe to eliminate the shortcomings as much as possible.

Scientific Hypothesis

It was anticipated that using iso-octane solvent in combination with floral and silica-based solid phase extraction cartridges for sample preparation would increase the method's selectivity. This approach will also simplify and reduce the cost of the GC/ECD method for determining selected polychlorinated biphenyls in fish roe and provide satisfactory metrological performance for evaluating its suitability.

MATERIAL AND METHODOLOGY

Samples

For the method's development and testing, we selected samples of salted black roe purchased at Kyiv (Ukraine) retail outlets. The authenticity of the roe samples was confirmed by determining their fatty acid composition.

Chemicals

PCB Test solution 14 for ECD 10 µg/mL in heptane, analytical standard. Product Number 33891. It contains the following components: PCB-No 18, PCB-No 28, PCB-No 31, PCB-No 44, PCB-No 52, PCB-No 101, PCB-No 118, PCB-No 138, PCB-No 149, PCB-No 153, PCB-No 170, PCB-No 180, PCB-No 194, PCB-No 208.

PCB No 209 solution in Isooctane 10 µg/mL is an analytical standard. Its product Number is 41612, and it is manufactured by Sigma Aldrich (Switzerland).

PCB No 30 solution in Isooctane 10 µg/mL, analytical standard. Product Number 72793, Sigma Aldrich (Switzerland).

Nitrogen gas of special purity, 99.999% (supplied by KRIOHENSERVIS LLC).

Isooctane for liquid chromatography LiChrosolv, Merck (Germany).

Sodium methoxide Natriummethoxid purum >97.0%, Fluka (Switzerland).

n-Hexan (purity GC 98%), Merck (Germany).

Methanol (HPLC grade), Lot: 1419984, Fisher Scientific (UK).

Chloroform for chromatography, Merck (Germany).

Diethyl ether (purity GC 98%), Merck (Germany).

Copure® Silica SPE Cartridge. Cat. No: Cosil61000, Biocomma (China).

Copure® Florisil SPE Cartridge. Cat. No: Cofl61000, Biocomma (China).

Biological Materials

To develop and test the methodology, we used black roe “Royal Caviar Classic”, 50 g, purchased from a retailer in one of the shopping centres in Kyiv.

Instruments

Solvent Extractor SER 148 (Soxclet apparatus); Velp Scientifica (Italy); Gas-liquid chromatography Trace GC Ultra, Thermo Fisher Scientific (United States); electron capture detector (ECD); capillary chromatography column SGE HT8-PCB (60 m× 0.25 mm, Part number 054236), Trajan Scientific and Medical; Vacuum manifold for solid-phase extraction with stand and vacuum pump N86 KT18, Laboport (France); Electronic laboratory scales Kern&Sohn GmbH ABJ 220-4M, KERN&SOHN (Germany); Shaking machine VortexMS 3 digital, IKA (Germany).

Laboratory Methods

The validation was performed at the Ukrainian Laboratory of Quality and Safety of Agricultural Products of the National University of Life and Environmental Sciences of Ukraine (accredited according to DSTU ISO/IEC 17025:2019). The suitability of our developed method for determining PCBs in fish roe was evaluated according to the established general and specific requirements for PCB determination, which are applied during validation. This evaluation considered requirements for sample collection and the formation of a composite sample, sample storage conditions, personnel competence, and the requirements for laboratory equipment, reagents, and the laboratory's microclimate. Additionally, certificates from an authorised institution confirm the calibration of the instruments. The requirements for linearity testing and constructing a calibration curve (which includes 5 calibration points, each in 3 repetitions) were met. During the validation, the following method requirements were ensured: Low working range and limits of quantification (For most PCB congeners limit of quantification in the nanogram (10 – 9 g) range is already sufficient); High selectivity (specificity); High accuracy; Limit of quantification (for a confirmatory method shall be about one-fifth of the maximum level); the relative standard deviation (RSD, %) of the measurement results under convergence conditions within (RSD ≥15%); the recovery percentage (R, 80 – 120%); the correlation coefficients (R^2 ≥0.995) **[34]**, **[35]**.

Following the quality system requirements of DSTU ISO/IEC 17025:2019 and following the Commission Decision and Commission Regulation **[34]**, **[35]**, the following microclimate conditions were ensured in the laboratory premises during testing: temperature: 20±5°C; humidity: <80%; atmospheric pressure range: 84.0 – 106.7 kPa. All reagents and analytical standards were within their valid storage period at the testing time, meaning they were not expired. The fish roe samples were stored in a refrigerator at 2 – 8°C temperature before analysis. The prepared test samples were stored for 7 days in hermetically sealed vials. PCB analytical standards were stored at a temperature of minus 18°C. Adhering to the microclimate conditions of the laboratory premises and the storage conditions of reagents and test samples is a key requirement in the method's suitability assessment. Therefore, the method's reliability was verified only under the conditions specified by the DSTU ISO/IEC 17025:2019 quality system and the Commission Decision and Commission Regulation **[34]**, **[35]**. No deviations from the specified microclimate and storage conditions were allowed during the method suitability assessment.

Description of the Experiment

Sample preparation: Fish roe samples were homogenised to a uniform mass. 5±0.1 g of fish roe was weighed and transferred to a cellulose cartridge for extraction. A layer of cotton wool was placed over the sample, and PCBs were extracted using a Soxhlet apparatus. The extraction (fat extraction) was performed at 80 °C – 30 min in diethyl ether, 60 min over ether and 30 min diethyl ether evaporation. 2 ml of isooctane was added to the dry residue of the extract, shaken vigorously for 1 min and transferred to 5 ml test tubes. A second portion of isooctane (2 ml) was added, shaken vigorously for 1 min, and the extract was combined in a 5 ml test tube. The extract was then purified by solid phase extraction using two cartridges: the upper one - Florisil SPE cartridge, the lower one - Silica SPE cartridge. The cartridges were conditioned with 2 ml of isooctane, and the extract was applied to the upper cartridge (Florisil SPE). Elution was performed with isooctane (3 times with 2 ml). The purified extracts obtained were made up to a volume of 10 ml and analysed by gas-liquid chromatography with an electron capture detector (ECD) using the chromatographic conditions recommended by the manufacturer of the SGE HT8-PCB capillary chromatography column on which the separation of PCBs was carried out.

Number of samples analyzed: 20 samples of fish roe.

Number of repeated analyses: 2.

Number of experiment replications: the number of replications of each experiment to determine a value was two.

Design of the experiment: In the first stage, we developed a method that included optimising sample preparation (optimal solvents, sample cleaning consumables) and selecting chromatographic conditions.

To determine the PCB content, a gas-liquid chromatograph Trace GC Ultra, Thermo Fisher Scientific (United States), and electron capture detector (ECD) were used. PCBs were separated on an SGE HT8-PCB capillary chromatography column (60 m × 0.25 mm, part number 054236).

Description of instrument settings and chromatographic conditions:

Injection volume – 2 µl, injection type – splitless; carrier gas type – nitrogen, flow rate – 2 ml/min, flow mode: constant flow. Temperature program for the GC oven:

Initial temperature – 70 °C, Hold time (minutes) – 1.00;

Ramp 1: Rate (°C/min) – 40.0, temperature (°C) – 130, Hold Time (minutes) – 0.00;

Ramp 2: Rate (°C/min) – 2.5, temperature (°C) – 290, Hold Time (minutes) – 5.00.

Oven Run-Time (min) – 71.50. Prep Run Timeout (min): 10.00. Equilibration Time (min): 0.50.

An Electron-Capture Detector (ECD) from Thermo Fisher Scientific was used. Description of the detector settings: Base Temperature (°C) – 300, ECD Temperature (°C) – 300, Reference Current (nA): 1.0, Pulse Amplitude (V) – 50, Pulse Width (µsec): 1.0. Makeup Flow (ml/min): 40.

Results were evaluated using the specialised instrument software Xcalibur. The mass fraction of each PCB was calculated using the external standard method and expressed in mg/kg. The second step was to assess the suitability of this method, i.e. its validation according to the following criteria: selectivity, linearity, limits of detection (LOD), limits of quantification (LOQ), accuracy and precision, and recovery. The suitability assessment of the method was carried out by Commission Regulation (EU) No 589/2014 **[34]** and Commission Decision 2002/657/EC **[35]**, which ensures the implementation of EU Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results **[36]**.

The limits of detection (LOD) for each PCB were calculated as the mass concentration of the component that produces a signal (peak area) that is 3 times higher than the signal of the blank sample (matrix). The limits of quantification (LOQ) for each PCB were calculated as the mass fraction of the component that produces a signal (peak area) that is 10 times higher than the signal of the control sample of the analyzed matrix **[34]**, **[35]**.

Statistical Analysis

The results were evaluated using the dedicated gas chromatography software Xcalibur, version 2.0.7 (Thermo Scientific Software). This programme consists of several separate blocks (Processing Setup, Quan Browser-Calibration) and allows automatic identification of component peaks by their release time and determination of linearity (R^2 calculation) during calibration. One of the functions of Xcalibur is also the export of primary data (retention times (Rt) PCBs, peak areas (S) and noise/signal (S/N)) to Microsoft Excel. To perform statistical analysis of the validation criteria and to determine the Relative Standard Deviation (RSD), Mean, Standard Square Deviation and Expanded Uncertainty, the appropriate formulae were written in Microsoft Excel. That is, statistical data analysis was performed using Microsoft Excel and Xcalibur.

The measurement results were statistically processed according to the Sante 11312/2021 guideline, calculating only the RSD (Relative Standard Deviation) in percentages. Calculating p-values is not a mandatory criterion when validating chromatographic methods **[37]**.

RESULTS AND DISCUSSION

The GC/MS method **[38]** with the recommended QuEChERS sample preparation **[39]** should be considered for determining PCBs in high-fat foods. It allows fast and efficient extraction of residual amounts of target compounds and purification of the extract from matrix components **[40]**, **[41]**.

Researchers have optimised a method for determining polychlorinated biphenyls in fish based on accelerated extraction with acetone/n-hexane (1:1) solvents **[42]**.

The GC-ECD method is also used to determine PCBs with recoveries of 95.7 – 101% **[43]**.

Several variants of PCB determination methods are described in the scientific literature **[44]** and official regulatory documents **[45]**. One method is for determining 19 PCBs in solid matrices using a capillary chromatography column (30 m) with different diameters. The sample preparation steps for determining the 19 PCB congeners can be used to analyse and identify other congeners. Still, not all 209 PCB congeners can be identified using the chromatography columns and analytical procedures described in this method **[46]**.

There are also several methods for extracting solid samples to determine PCBs, which are listed in the official methods. Solid samples can be extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using Method 3540C (Soxhlet) **[47]**, Method 3541 (automated Soxhlet) **[48]**, Method 3545 (pressurised fluid extraction) **[49]**, Method 3546 (microwave extraction) **[50]**, Method 3550 B (ultrasonic extraction) **[51]**, Method 3562 (supercritical fluid extraction) **[52]**.

Capillary columns with an internal diameter of 0.25 mm, 0.32 mm or 0.53 mm are used for GC/ECD chromatography. Columns with smaller inner diameters have a higher chromatographic resolution than those with larger inner diameters. Chromatographic columns with a smaller inner diameter (0.25 mm) and long length (>60 m) can generally be more efficient in separating a larger number of PCB congeners **[53]**.

An analytical method has been developed based on the extraction of organochlorine pesticides (p,p'DDT, p,p'DDE, p,p'DDD, α-HCCG, β-HCCG, γ-HCCG, heptachlor) and PCBs with organic solvents, purification of the extracts obtained and subsequent quantitative determination of these compounds by GC/ECD **[45]**. A method for determining 6 PCBs in chicken eggs is also described. It involves extraction for 3 hours on a magnetic stirrer using n-hexane/acetone 85:15 (v:v), ultrasonication, evaporation under a nitrogen stream, addition of sulphuric acid and ENVI-carb®, overnight soaking, centrifugation, repeated evaporation under a nitrogen stream, addition of n-hexane solvent, purification with Bond Elut-PCB, repeated evaporation under a nitrogen stream and dissolution of the residue in isooctane **[54]**.

In the scientific literature **[26]**, a multi-step preparation of roe samples for GC/ECD analysis is described, involving 24-hour sample extraction using a Soxhlet apparatus, evaporation on a rotary evaporator, centrifugation and concentration of the sample under a nitrogen stream using reagents such as sodium sulphate, sulphuric acid, hexane and dichloromethane. Other methods for determining PCBs are also known and have advantages and disadvantages **[21]**.

At present, the scientific community working in the field of analytical methods development aims to find new methods, to develop simplified methods of sample preparation for the determination of PCBs in foods with high-fat content, which would be characterised by the shortest possible execution time, minimal use of human resources, require the use of small volumes of solvents, i.e. have a low cost, but at the same time provide effective extraction of the components of interest and acceptable metrological characteristics of the method **[40]**.

To overcome the disadvantages of traditional sample preparation (long and multi-step) **[28]**, **[29]**, **[30]**, **[31]**, **[55]** in the determination of PCBs in fish roe, we proposed a method for the determination of 14 PCBs in fish roe using automated Soxhlet extraction followed by purification of the extracts by solid phase extraction (SPE).

The essence of the method modification is the extraction of fat from fish roe with diethyl ether (using a Soxhlet apparatus), followed by SPE purification of the samples using 2 types of cartridges: Florisil SPE cartridge (pore volume 0.70 – 0.90 mL/g) and Silica SPE cartridge containing silicon dioxide (SiO_2), magnesium dioxide (MgO) and sodium dioxide (Na_2SO_4), using is ethane as eluent.

The sample preparation procedure for our modified method is described in this article's 'Sample preparation' section.

Assessment of method suitability. The method was validated according to the criteria of the European Commission Regulation (EU) No 589/2014 **[34]** and Commission Decision 2002/657/EC **[35]**: selectivity, linearity, limit of detection (LOD), limit of quantification (LOQ), precision and accuracy.

Optimisation of the chromatographic conditions allowed the determination of retention times (Rt) for all the PCBs analysed. Chromatogram of a 14-component analytical standard for PCBs (Rt for PCB 18 – 24.94; for PCB 31 – 28.79; for PCB 28 – 29.08; for PCB 52 – 31.32; for PCB 44 – 33.08; for PCB 101 – 38.36; for PCB 149 – 42.55; for PCB 118 – 43.90; for PCB 153 – 45.22; for PCB 138 – 47.25; for PCB 180 – 52.49; for PCB 170 – 54.49; for PCB 194 – 59.39; for PCB209 – 62.02) at the level of 0.01 mg/kg is shown in Figure 1.

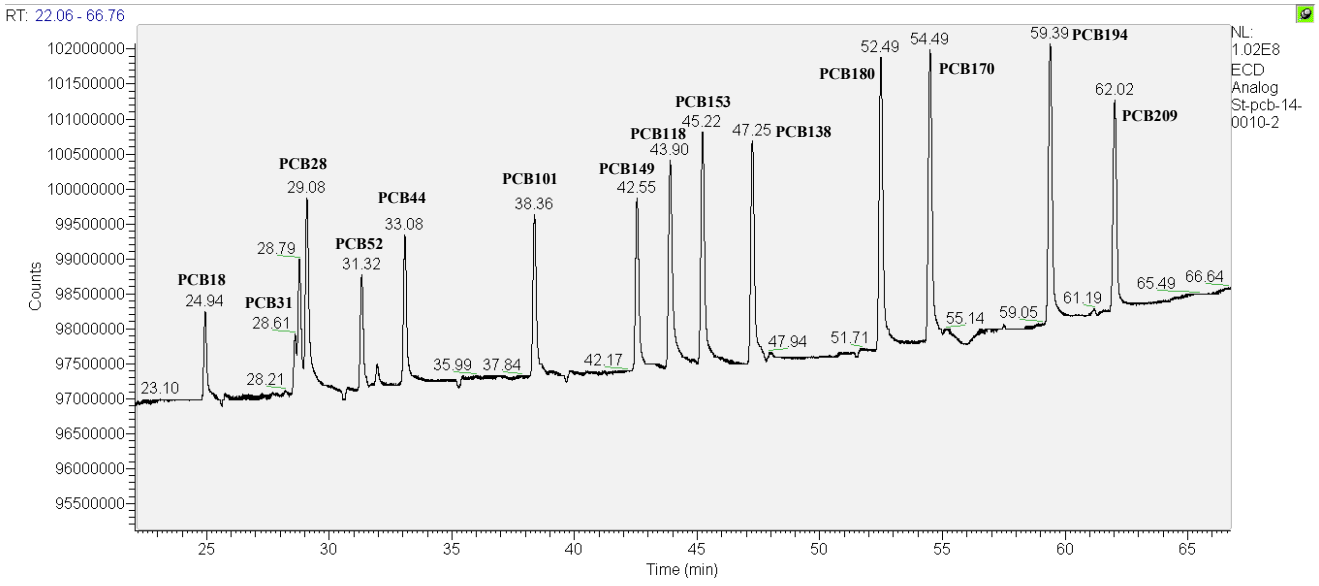

Figure 1 Chromatogram of analytical standard PCBs Test solution 14 for ECD (PCB 18, PCB 31, PCB 28, PCB 52, PCB44, PCB 101, PCB 149, PCB 118, PCB 153, PCB 138, PCB 180, PCB 170, PCB 194, PCB 209) at 0.01 mg/kg.

Selectivity. To determine the selectivity of the method, samples of black salted fish roe free of PCBs (blank samples) and simulated samples containing 14 PCBs (PCB 18, PCB 31, PCB 28, PCB 52, PCB 44, PCB 101, PCB 149, PCB 118, PCB 153, PCB 138, PCB 180, PCB 170, PCB 194, PCB 209) at concentrations of 0.005 mg/kg, 0.01 mg/kg, 0.02 mg/kg; 0.04 mg/kg were analysed. A comparison of the chromatograms obtained showed that the determination of PCBs in fish roe was not affected by other components in the sample (Figur 2). It should also be noted that gas-liquid chromatography with an electron capture detector (GC/ECD) is a highly selective

method, allowing the determination of an analyte in the presence of matrix components due to the operation of the detector **[26]**.

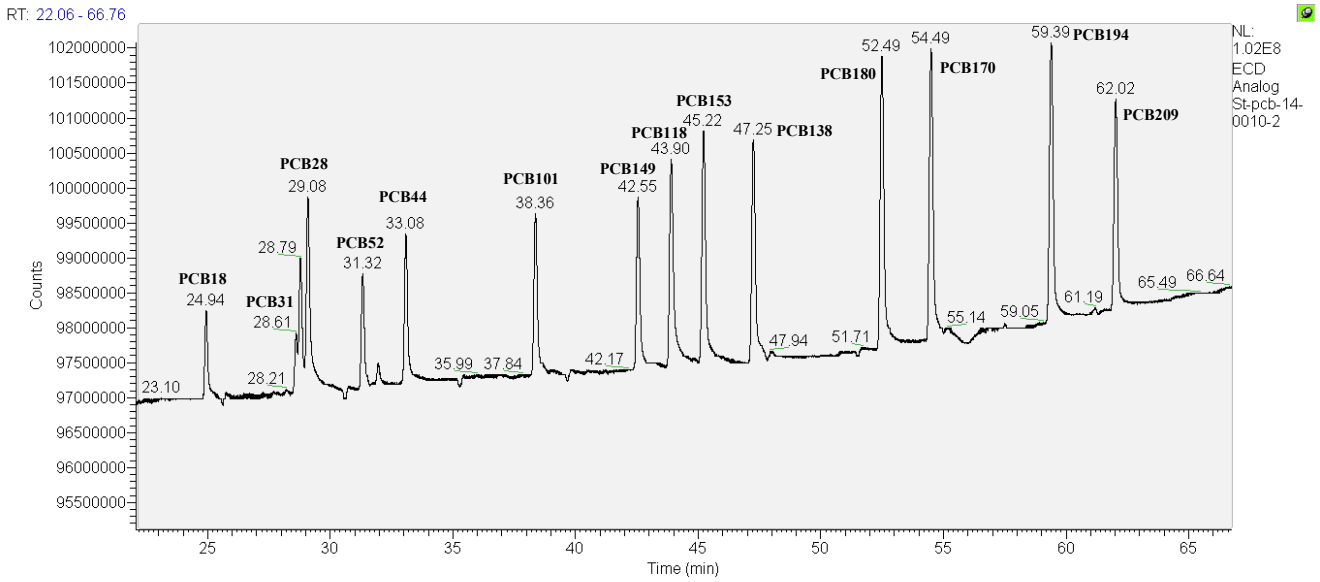

Figure 2 Chromatogram of added 14 PCBs in a model fish roe sample at 0.01 mg/kg.

Table 1 Results of the evaluation of linearity, limit of detection and limit of quantification of the developed method.

Name according to IUPAC[1] nomenclature	Linear range, mg/kg	R^2	LOQ, mg/kg	LOD, mg/kg
2,2',5-Trichlorobiphenyl (PCB18)	0.002 – 0.050	0.9988	0.003	0.0009
2,4',5-Trichlorobiphenyl (PCB31)	0.002 – 0.050	0.9990	0.001	0.0003
2,4,4'-Trichlorobiphenyl (PCB 28)	0.002 – 0.050	0.9966	0.001	0.0003
2,2',5,5'-Tetrachlorobiphenyl (PCB 52)	0.002 – 0.050	0.9991	0.001	0.0003
2,2',3,5'-Tetrachlorobiphenyl (PCB44)	0.002 – 0.050	0.9984	0.001	0.0003
2,2',4,5,5'-Pentachlorobiphenyl (PCB101)	0.002 – 0.050	0.9999	0.001	0.0003
2,2',3,4',5',6-Hexachlorobiphenyl (PCB149)	0.002 – 0.050	0.9993	0.001	0.0003
2,3',4,4',5-Pentachlorobiphenyl (PCB118)	0.002 – 0.050	0.9989	0.001	0.0003
2,2',4,4',5,5'-Hexachlorobiphenyl (PCB153)	0.002 – 0.050	0.9979	0.001	0.0003
2,2',3,4,4',5'-Hexachlorobiphenyl (PCB138)	0.002 – 0.050	0.9972	0.001	0.0003
2,2',3,4,4',5,5'-Heptachlorobiphenyl (PCB180)	0.002 – 0.050	0.9978	0.001	0.0003
2,2',3,3',4,4',5-Heptachlorobiphenyl (PCB170)	0.002 – 0.050	0.9998	0.001	0.0003
2,2',3,3',4,4',5,5'-Octachlorobiphenyl(PCB194)	0.002 – 0.050	0.9962	0.001	0.0003
2,2′,3,3′,4,4′,5,5′,6,6′-Decachlorobiphenyl(PCB209)	0.002 – 0.050	0.9974	0.001	0.0003

Note: IUPAC[1] – International Union of Pure and Applied Chemistry; R^2 – correlation coefficients.

Linearity. To establish the calibration curve, 5 solutions of the analytical standard 14 PCBs with the specified PCB concentrations (0.05 mg/kg, 0.02 mg/kg, 0.01 mg/kg, 0.005 mg/kg, 0.002 mg/kg) were used. For each standard solution, two values of the analytical signal (chromatographic peak area) were obtained using one batch of reagents, equipment and consumables. Regression analysis of the data was performed by the least squares method using a linear model.

The calibration curves for all PCBs showed R^2 values ranging from 0.9962 to 0.9999, which meets the required level of ≥0.995 (Table 1, Figure 3 and Figure 4).

Therefore, the standard curves for polychlorinated biphenyls (PCB 18, PCB 31, PCB 28, PCB 52, PCB 44, PCB 101, PCB 149, PCB 118, PCB 153, PCB 138, PCB 180, PCB 170, PCB 194, PCB 209) are linear in the range 0.002 to 0.05 mg/kg.

Limits of detection (LOD). The limit of detection for each of the 14 PCBs was determined based on the signal-to-noise ratio (S/N) of the chromatographic peak, which is three times higher than the S/N of the blank sample (S/N = 3).

The results showed that the limit of detection for PCBs in fish roe was 0.0009 mg/kg for PCB 18 and 0.0003 mg/kg for PCB 31, PCB 28, PCB 52, PCB 44, PCB 101, PCB 149, PCB 118, PCB 153, PCB 138, PCB 180, PCB 170, PCB 194, PCB 209 (Table 1).

Limits of quantification (LOQ). The limit of quantification for each PCB was determined based on the signal-to-noise ratio (S/N) of the chromatographic peak, which is 10 times higher than the S/N of the blank (S/N=10).

It was found that the limit of quantification (LOQ) of PCBs in fish roe was 0.003 mg/kg for PCB 18 and 0.001 mg/kg for PCB 31, PCB 28, PCB 52, PCB 44, PCB 101, PCB 149, PCB 118, PCB 153, PCB 138, PCB 180, PCB 170, PCB 194, PCB 209 (Table 1).

According to the current regulatory document in Ukraine **[22]** and EU Commission Regulation (EU) No 1259/2011 **[23]**, the total amount of six PCBs (PCB 28, PCB 52, PCB 101, PCB 138, PCB 153 and PCB 180) in fish products (including roe) should not exceed 75 ng/g (0.075 mg/kg).

Therefore, the limit of detection and limit of quantification of polychlorinated biphenyls according to the developed method is acceptable for their determination in fish roe by the regulatory documents of Ukraine and EU Commission Regulation No. 589/2014 **[34]**.

Accuracy. The accuracy of PCB determination in fish roe was evaluated using the injected-found method. The analytical standard of 14 PCBs (PCB 18, PCB 31, PCB 28, PCB 52, PCB 44, PCB 101, PCB 149, PCB 118, PCB 153, PCB 138, PCB 180, PCB 170, PCB 194, PCB 209) at levels of 0.005, 0.01, 0.02 and 0.04 mg/kg was added to the fish roe samples which did not contain residual PCBs. After all the steps of sample preparation and GC/ECD analysis of the extracts obtained, the concentration of PCBs was determined and the degree of recovery (R, %) was calculated for 5 model matrices of artificially enriched PCBs.

The results of the study showed that the lowest recovery (R, %) of PCBs at the level of 0.01 mg/kg was obtained for PCB 31, which was 81.50%; the highest recovery was obtained for PCB 118, which was 107% (at an added concentration of 0.02 mg/kg), and for PCB170, which was 106.75% (at an added concentration of this PCB of 0.04 mg/kg) (Table 2).

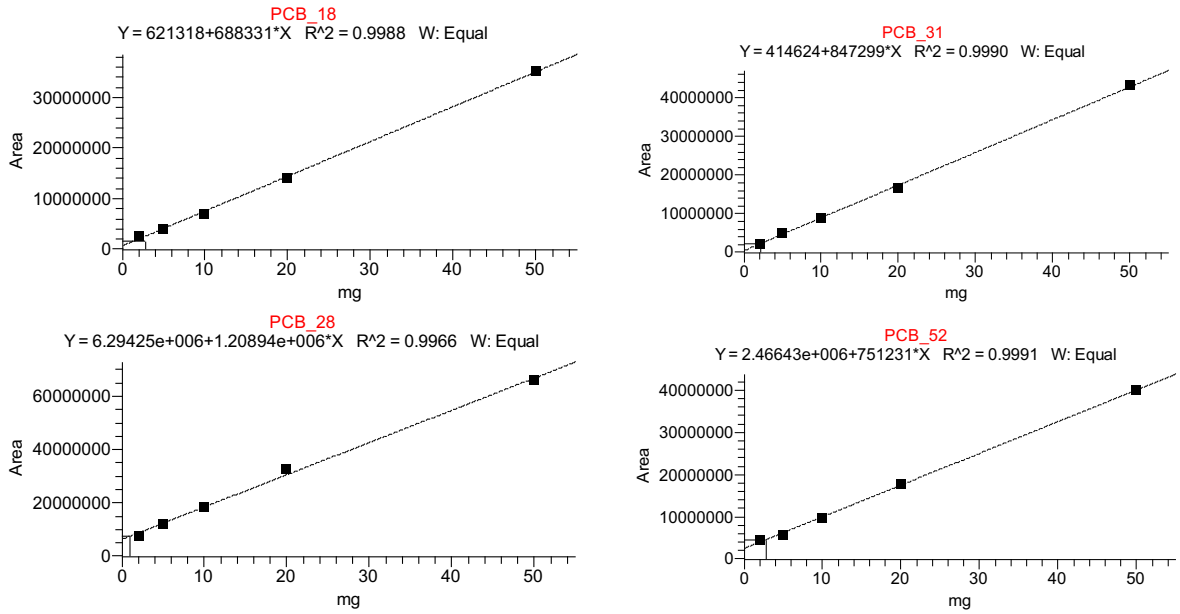

Figure 3 Linearity of solutions of 5 concentrations of the PCBs analytical standard (PCB 18, 28, 31 and 52).

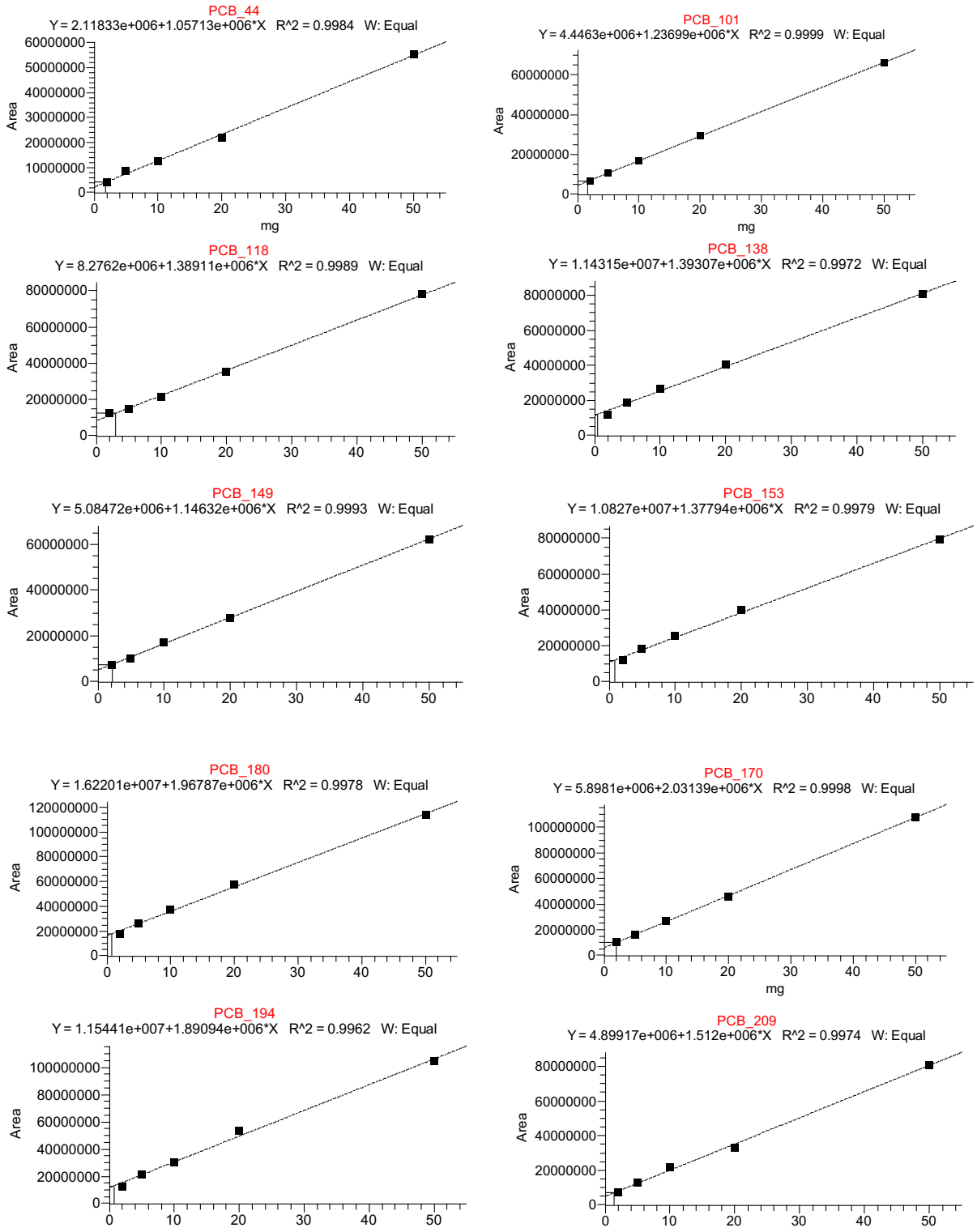

Figure 4 Linearity of solutions of 5 concentrations of the PCBs analytical standard (PCB: 44, 101, 118, 138, 149, 153, 170, 180, 194, 209).

Table 2 Results of the evaluation of the accuracy and precision of the determination of 14 PCBs (n=5).

PCBs	The concentration of PCBs added to the sample							
	0.005 mg/kg		0.01 mg/kg		0.02 mg/kg		0.04 mg/kg	
	[1]R, %	[2]RSD, %	[1]R, %	[2]RSD, %	[1]R, %	[2]RSD, %	[1]R, %	[2]RSD, %
PCB18	99.40	4.29	92.00	4.84	95.00	7.07	91.23	2.66
PCB31	100.00	2.83	81.50	5.24	93.50	4.54	99.06	1.02
PCB28	102.00	2.77	99.65	1.92	94.25	4.88	88.75	5.98
PCB52	88.60	9.43	89.50	5.53	96.75	2.56	99.75	1.42
PCB44	94.00	6.02	99.50	7.82	99.00	1.43	97.50	2.90
PCB101	90.00	3.14	93.00	6.08	97.50	2.15	96.63	1.79
PCB149	95.00	4.47	99.90	6.21	104.00	1.36	100.88	1.60
PCB118	104.00	2.72	107.00	1.32	106.75	2.09	102.13	1.56
PCB153	101.00	1.40	101.00	1.40	103.00	3.47	103.25	1.37
PCB138	97.00	1.46	98.00	1.44	96.80	5.29	99.00	2.96
PCB180	99.80	4.10	101.50	2.21	102.00	1.69	103.00	2.40
PCB170	100.00	6.84	99.50	5.42	101.75	1.04	106.75	1.85
PCB194	100.50	7.44	101.50	4.56	101.25	1.05	93.38	1.33
PCB209	100.70	1.83	98.50	2.15	102.05	3.78	96.63	1.49

[1]R – degree of recovery; [2]RSD – relative mean square deviation.

Thus, the obtained results of the degree of PCB extraction from fish roe correspond to the range of permissible values (80 – 120%) given in the EU Commission Regulation No. 589/2014 **[34]**.

Precision. The precision of the GC/ECD method for the analysis of PCBs in fish roe was determined by the convergence of the measurement results. Convergence was estimated according to the following scheme:

- model (artificially spiked with PCBs at levels of 0.005, 0.01, 0.02 and 0.04 mg/kg) samples of black fish roe were analysed in 10 replicates;
- this experiment was performed under conditions of convergence (under the same conditions, with the same equipment, by the same researcher, within a short period);
- the relative standard deviation (RSD, %) values were calculated for the concentration values obtained.

It was found that the relative standard deviation (RSD, %) of the results of measurement of model fish roe samples under conditions of convergence for PCB at concentrations of 0.005 mg/kg, 0.01 mg/kg, 0.02 and 0.04 mg/kg for PCB 18 (2.66 – 7.07 %); for PCB 31 (1.02 – 5.24 %); for PCB 28 (1.92 – 5. 98 %); for PCB 52 (1.42 – 9.43 %); for PCB 44 (1.43 – 7.82 %); for PCB 101 (1.79 – 6.08 %); for PCB 149 (1.36 – 6.21 %); for PCB 118 (1.32 – 2. 72 %); for PCB 153 (1.37 – 3.47%); for PCB 138 (1.44 – 2.96%); for PCB 180 (1.69 – 4.10%); for PCB 170 (1.04 – 6.84%); for PCB 194 (1.05 – 7.44%); for PCB 209 (1.49 – 3.78%) (Table 2).

Thus, the relative standard deviation of the measurement results under convergence conditions ranged from 1.02% to 9.43%, which does not exceed the established values (RSD ≥15%) given in the EU Commission Regulation No. 589/2014 **[34]**. The results of the convergence evaluation indicated the absence of systemic errors in the developed methodology.

The evaluation of the suitability (validation) of the method for determining 14 PCBs (PCB 18, PCB 31, PCB 28, PCB 52, PCB 44, PCB 101, PCB 149, PCB 118, PCB 153, PCB 138, PCB 180, PCB 170, PCB 194, PCB 209) in fish roe by GC/ECD using automated Soxhlet extraction followed by purification of the extracts by SPE (Florisil, Silica) showed acceptable metrological characteristics **[34]**.

Thus, the results obtained provide the basis for further studies on method modification using solvents and solid phase purification methods for the determination not only of PCBs in fatty products but also of other fat-soluble persistent organic pollutants, in particular polyaromatic hydrocarbons and organochlorine pesticides.

CONCLUSION

The method for the determination of polychlorinated biphenyls (PCB 18, PCB 31, PCB 28, PCB 52, PCB 44, PCB 101, PCB 149, PCB 118, PCB 153, PCB 138, PCB 180, PCB 170, PCB 194, PCB 209) in fish roe by gas-liquid chromatography with electron capture detector (GC/ECD) using automated Soxhlet extraction followed by purification of the extracts by SPE (Silica, Florisil SPE cartridges) showed acceptable metrological characteristics. The correlation coefficients (R^2) for PCBs were ≥0.995. The limit of detection (LOD) and limit of quantification (LOQ) of PCBs were below the European Union (EU) limits. The recovery of PCBs from fish roe ranged from 81.5% to 107%, indicating the proposed method's acceptability (R, 80 – 120%). The relative standard deviation of the recovery results ranged from 1.02% to 9.43%. These values do not exceed the established standards, as specified in the EU Regulation No. 589/2014. The results of the studies give grounds to believe that the method developed by GC/ECD for the determination of 14 polychlorinated biphenyls (PCB 18, PCB 31, PCB 28, PCB 52, PCB 44, PCB 101, PCB 149, PCB 118, PCB 153, PCB 138, PCB 180, PCB 170, PCB 194, PCB 209) in fish roe meets the requirements of Commission Regulation (EU) No 589/2014 and is suitable for use in specialised chemical analytical laboratories for food safety control.

REFERENCES

1. Holembovska, N., Tyshchenko, L., Slobodyanyuk, N., Israelian, V., Kryzhova, Y., Ivaniuta, A., Pylypchuk, O., Menchynska, A., Shtonda, O., & Nosevych, D. (2021). Use of aromatic root vegetables in the technology of freshwater fish preserves. In Potravinarstvo Slovak Journal of Food Sciences (Vol. 15, pp. 296–305). HACCP Consulting. https://doi.org/10.5219/1581
2. Makarenko, A., Mushtruk, M., Rudyk-Leuska, N., Kononenko, R., Shevchenko, P., Khyzhniak, M., Martseniuk, V., Kotovska, G., Klymkovetskyi, A., & Glebova, J. (2022). Investigation of internal organs and additive tissue of hybrid hypophthalmichthys (Hypophthalmichthys spp.) as a promising raw material for the production of dietary nutritional products. In Potravinarstvo Slovak Journal of Food Sciences (Vol. 16, pp. 411–430). HACCP Consulting. https://doi.org/10.5219/1760
3. Bondarchuk, M., Khartii, M. (2022). Global trends in the development of the caviar products market. In Efektyvna ekonomika (Vol. 2, pp. 1–9). Dnipro State Agrarian and Economic University. https://doi.org/10.32702/2307-2105-2022.2.77
4. Overview of the fish market of Ukraine for 2022 and 2023. (2024, January, 4). In UIFSA. https://uifsa.ua/news/news-of-ukraine/overview-of-the-fish-market-of-ukraine-for-2022-and-2023
5. Makarenko, A., Mushtruk, M., Rudyk-Leuska, N., Kononenko, I., Shevchenko, P., Khyzhniak, M., Martseniuk, N., Glebova, J., Bazaeva, A., & Khalturin, M. (2021). The study of the variability of morphobiological indicators of different size and weight groups of hybrid silver carp (Hypophthalmichthys spp.) is a promising direction of development of the fish processing industry. In Potravinarstvo Slovak Journal of Food Sciences (Vol. 15, pp. 181–191). HACCP Consulting. https://doi.org/10.5219/1537
6. Bunga, S., Carne, A., Bekhit, A. El-D. A. (2022). Chapter 3 - Composition and nutrition of fish roes. In Bekhit, A. El-D. A. (Ed.), Fish roe: Biochemistry, Products, and Safety (pp. 41–92). Academic Press. https://doi.org/10.1016/B978-0-12-819893-3.00011-4
7. Wirth, M., Kirschbaum, F., Gessner, J., Krüger, A., Patriche, N., Billard, R. (2000). Chemical and biochemical composition of caviar from different sturgeon species and origins. In Nahrung (Vol. 44, Issue 4, pp. 233–237). Akademie-Verlag.
8. Bal'-Prylypko, L. V., Derevyanko, L. P., Slobodyanyuk, N. M., Starkova, E. R., & Androshchiuk, O. S. (2018). Using of the Ampullaria glauca snails' caviar for correction of the effects of the ionizing radiation exposure in small dose. In Nuclear Physics and Atomic Energy (Vol. 19, Issue 2, pp. 159–165). National Academy of Sciences of Ukraine (Co. LTD Ukrinformnauka) (Publications). https://doi.org/10.15407/jnpae2018.02.159
9. Ugnivenko, A., Nosevych, D., Antoniuk, T., Chumachenko, I., Ivaniuta, A., Slobodyanyuk, N., Kryzhova, Y., Rozbytska, T., Gruntovskyi, M., & Marchyshyna, Y. (2022). Manifestation of living and post-slaughter traits of productivity in inbred and outbred bull calves of Ukrainian meat cattle breed. In Potravinarstvo Slovak Journal of Food Sciences (Vol. 16, pp. 356–366). HACCP Consulting. https://doi.org/10.5219/1769
10. Honchar, V., Iakubchak, O., Shevchenko, L., Midyk, S., Korniyenko, V., Kondratiuk, V., Rozbytska, T., Melnik, V., & Kryzhova, Y. (2022). The effect of astaxanthin and lycopene on the content of fatty acids in the yolks of chicken eggs under different storage regimes. In Potravinarstvo Slovak Journal of Food Sciences (Vol. 16, pp. 473–489). HACCP Consulting. https://doi.org/10.5219/1774
11. Gong, Ya., Huang, Ya., Gao, L., Lu, J., Hu, Yu., Xia, L., Huang, H. (2013). Nutritional Composition of Caviar from Three Commercially Farmed Sturgeon Species in China. In Journal of Food and Nutrition Research (Vol. 1, Issue 5, pp. 108–112). Graduate School Foundation Inc.

12. Ma, S., Li, L., Hao, S., Yang, X., Huang, H., Cen, J., Wang Yu. (2020). Journal of Oleo Science (Vol. 69, Issue 10, pp.1199–1208). Japan Oil Chemists' Society. https://doi.org/10.5650/jos.ess20061
13. Abbas, E., Hrachya, G. (2015). Fatty acid composition of caviar and liver from cultured great sturgeon (Huso huso). In International Food Research Journal (Vol. 22, Issue 3, pp.1083–1086). Elsevier BV.
14. Ivaniuta, A., Menchynska, A., Nesterenko, N., Holembovska, N., Yemtcev, V., Marchyshyna, Y., Kryzhova, Y., Ochkolyas, E., Pylypchuk, O., & Israelian, V. (2021). The use of secondary fish raw materials from silver carp in the technology of structuring agents. In Potravinarstvo Slovak Journal of Food Sciences (Vol. 15, pp. 546–554). HACCP Consulting. https://doi.org/10.5219/1626
15. DSTU 8096, 2015. Salted fish roe. Specifications.
16. Khyzhnyak, S., Voitsitskiy, V., Korniyenko, V. (2022). Polychlorinated biphenyls in the environment and methods of their determination. In Topical issues of the development of veterinary medicine and breeding technologies: scientific monograph (pp. 546–570). Baltija Publishing. https://doi.org/10.30525/978-9934-26-258-6-17
17. Shang, X., Dong, G., Zhang, H., Zhang, L., Yu, X., Li, J., Wang, X., Yue, B., Zhao, Y., Wu, Y. (2016). Polybrominated diphenyl ethers (PBDEs) and indicator polychlorinated biphenyls (PCBs) in various marine fish from Zhoushan fishery, China. In Food Control (Vol. 67, pp. 240–246). EFFoST. https://doi.org/10.1016/j.foodcont.2016.03.008.
18. Panesar, H. K., Kennedy, C. L., Keil, Stietz, K. P., Lein, P. J. (2020). Polychlorinated Biphenyls (PCBs): Risk Factors for Autism Spectrum Disorder? In Toxics (Vol. 8, pp. 1–32). MDPI AG. https://doi.org/10.3390/toxics8030070
19. Abolghasemi, M., Esmaeilzadeh, S., Mirabi, P., Golsorkhtabaramiri, M. (2021). Human Exposure to Polychlorinated Biphenyls (PCBs) and The Risk of Endometriosis: A Systematic Review and Meta-Analysis Protocol. In International Journal of preventive medicine (Vol. 12, p. 108). Isfahan University of Medical Sciences. https://doi.org/10.4103/ijpvm.IJPVM_178_19
20. Bober, A., Liashenko, M., Protsenko, L., Slobodyanyuk, N., Matseiko, L., Yashchuk, N., Gunko, S., & Mushtruk, M. (2020). Biochemical composition of the hops and quality of the finished beer. In Potravinarstvo Slovak Journal of Food Sciences (Vol. 14, pp. 307–317). HACCP Consulting. https://doi.org/10.5219/1311
21. Liu, J., Li, G., Liu, J., Wang, P., Wu, D., Zhang, X., & Wu, Y. (2023). Recent Progress on Toxicity and Detection Methods of Polychlorinated Biphenyls in Environment and Foodstuffs. In Critical Reviews in Analytical Chemistry (Vol. 53, Issue 4, pp. 928–953). Taylor & Francis. https://doi.org/10.1080/10408347.2021.1997570
22. State sanitary rules and standards. (2020). Maximum permissible levels of certain pollutants in food products. Order No. 1238 dated 05.22.2020. Retrieved from: https://zakon.rada.gov.ua/laws/show/z0684-20#Text
23. Commission Regulation (EU) No 1259. (2011). Commission Regulation (EU) No 1259/2011 of 2 December 2011 amending Regulation (EC) No 1881/2006 as regards maximum levels for dioxins, dioxin-like PCBs and non dioxin-like PCBs in foodstuffs. In Official Journal of the European Union (Vol. 3, pp. 18–23). Publications Office of the European Union.
24. Lüth, A., Lahrssen-Wiederholt, M., Karl, H. (2018). Studies on the influence of sampling on the levels of dioxins and PCB in fish. In Chemosphere (Vol. 212, pp. 1133–1141). Elsevier BV. https://doi.org/10.1016/j.chemosphere.2018.09.011
25. Eghbaljoo, H., Ghalhari, M. R., Shariatifar, N., Khaniki, G. J., Aghaee, E. M., Sani, M. A., Mansouri, E., Majid Arabameri (2023). Analysis of polychlorinated biphenyls (PCBs) in edible oils using the QuEChERS/GC-MS method: A health risk assessment study. In Heliyon (Vol. 9, p. 21317). Elsevier BV. https://doi.org/10.1016/j.heliyon.2023.e21317
26. Grafton, A., Lee, D., Libero, D., Miller, J., Rapko, K. (2006). Polychlorinated Biphenyls (PCBs) in Fish Roe. In Journal of Young Investigators (Vol. 1). Philadelphia University. Retrieved from: https://www.jyi.org/2006-january/2017/10/8/polychlorinated-biphenyls-pcbs-in-fish-roe
27. Colangelo, R., Diletti, G., Scortichini, G., Calitri, A., Casamassima, F., Iammarino, M., Nardelli, V., Zianni, R., Ingegno, M. (2023). Determination of non-dioxin like polychlorinated biphenyls by GC-ECD and GC-HRMS analysis in seafood. Conference: Chimica sotto l'Albero 2023 - Innovazione e Resilienza: Giovani Ricercatori per un Futuro Sostenibile.
28. DSTU EN 1528-1, 2002. Fatty food products. Determination of pesticides and polychlorinated biphenyls (PCB). Part 1. General provisions (EN 1528-1:1996, IDT).
29. EN 1528-2, 1998. Fatty food. Dnetermination of pesticides and polychlorinated biphenyls (PCBs). Part 2: Extraction of fat, pesticides and PCBs, and determination of fat content
30. EN 1528-3, 1996. Fatty food. Determination of pesticides and polychlorinated biphenyls (PCBs). Part 3. Clean-up methods.

31. EN 1528-4, 1996. Fatty food. Determination of pesticides and polychlorinated biphenyls (PCBs). Part 4: Determination, confirmatory tests, miscellaneous.

32. BS EN 1528-3, 1997. Fatty food. Determination of pesticides and polychlorinated biphenyls (PCBs) Clean-up methods Retrieved from: https://www.epa.gov/sites/default/files/2015-12/documents/8082a.pdf

33. Commission Regulation (EU) No 589. (2014). Commission Regulation (EU) No 589/2014 of 2 June 2014 laying down methods of sampling and analysis for the control of levels of dioxins, dioxin-like PCBs and non-dioxin-like PCBs in certain foodstuffs and repealing Regulation (EU) No 252/2012. In Official Journal of the European Union (Vol. 3, pp.18–40). Publications Office of the European Union.

34. Commission Decision of 14 August 2002 implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results (notified under document number C (2002) 3044), text with EEA relevance 2002/657/ EC. In Official journal of the European Union (L 221, pp. 8–36).

35. Council Directive 96/23/EC of 29 April 1996 on measures to monitor certain substances and residues there of in live animals and animal products and repealing Directives 85/358/EEC and 86/469/EEC and Decisions 89/187/EEC and 91/664/EEC.

36. SANTE 11312/2021 (2021). Analytical quality control and method validation procedures for pesticide residues analysis in food and feed. Retrieved from: https://www.eurl-pesticides.eu/userfiles/file/EurlALL/SANTE_11312_2021.pdf

37. Levchuk, I. V. (2014). Determination of polychlorinated biphenyls (PCBs) in oils and fats. In Intehrovani Tekhnolohii ta Enerhozberezhennya (Vol. 1, pp. 113–120). National Technical University "Kharkiv Polytechnic Institute".

38. Ostadgholami, M., Zeeb, M., Amirahmadi, M., Daraei, B. (2024). Multivariate Optimization and Validation of a Modified QuEChERS Method for Determination of PAHs and PCBs in Grilled Meat by GC-MS. In Foods (Vol. 13, p. 143). Multidisciplinary Digital Publishing Institute (MDPI). https://doi.org/10.3390/foods13010143

39. Chmil, V. D., Golohova, O. V., Vydrin, D. J., Kalashnikov, A. A. (2016). Prospects of using the QuEChERS method to assess the toxicological safety of food products. In Problemy harchuvannja (Vol. 2, pp. 69–78). Scientific center of preventive toxicology, food and chemical safety named after Academician LI Medved.

40. Senin, S. A., Midyk, S. V., Kornienko, V. I., Konovalova, O.Yu., Berezovskiy, O. V., Ladohubets, E. V., Harkusha, I. V. (2023). Determination of Mycotoxins in Wheat Grain by LC-MS/MS using Modified QuEChERS Sample Preparation. In Methods and Objects of Chemical Analysis (Vol. 18, Issue 1, p. 22–28). Taras Shevchenko National University of Kyiv. https://doi.org/10.17721/moca.2023.22-28

41. Ottonello, G., Ferrari, A., Magi, E. (2014). Determination of polychlorinated biphenyls in fish: Optimisation and validation of a method based on accelerated solvent extraction and gas chromatography–mass spectrometry. In Food Chemistry (Vol. 142, pp. 327–333). Elsevier BV. https://doi.org/10.1016/j.foodchem.2013.07.048

42. Afful, S., Awudza, J. A. M., Twumasi, S. K., Osae, S. (2013). Determination of indicator polychlorinated biphenyls (PCBs) by gas chromatography–electron capture detector. In Chemosphere (Vol. 93, Issue 8, pp. 1556–1560). Elsevier BV. https://doi.org/10.1016/j.chemosphere.2013.08.001

43. Skrynnyk M.M. (2017). Determination of organochlorine pesticides and polychlorinated biphenyls in aquatic organisms by chromato-mass-spectrometry method. [Candidate dissertation, Uzhgorod National University]. Uzhgorod National University. Retrieved from: https://www.uzhnu.edu.ua/uk/infocentre/get/11325

44. DSTU 4514, 2006. Fish, other water fresh resources and food stuffs from them. Detection of chlorine-organik pesticids and polychlorinated bifenils by method of gas-liquid chromatography.

45. Method 8082A. (2000). Polychlorinated biphenyls (PCBs) by gas chromatography. https://www.accustandard.com/media/assets/8082a.pdf

46. Method 3540C. (1996). Soxhlet extraction. Retrieved from: https://www.epa.gov/sites/default/files/2015-12/documents/3540c.pdf

47. Method 3541. (1994). Automated Soxhlet extraction. Retrieved from: https://www.epa.gov/sites/default/files/2015-06/documents/epa-3541.pdf

48. Method 3545. (1996). Pressurized fluid extraction (PFE). Retrieved from: http://www.cromlab.es/Articulos/Metodos/EPA/3000/3545.PDF

49. Method 3546. (2007). Microwave extraction. Retrieved from: https://www.epa.gov/sites/default/files/2015-12/documents/3546.pdf

50. Method 3550 B. (1996). Ultrasonic extraction. http://www.cromlab.es/Articulos/Metodos/EPA/3000/3550B.PDF

51. Method 3562. (2007). Supercritical fluid extraction of polychlorinated biphenyls (PCBs) and organochlorine pesticides. Retrieved from: https://www.epa.gov/sites/default/files/2015-12/documents/3562.pdf

52. Zheplinska, M., Mushtruk, M., Vasyliv, V., Sarana, V., Gudzenko, M., Slobodyanyuk, N., Kuts, A., Tkachenko, S., & Mukoid, R. (2021). The influence of cavitation effects on the purification processes of beet sugar production juices. In Potravinarstvo Slovak Journal of Food Sciences (Vol. 15, pp. 18–25). HACCP Consulting. https://doi.org/10.5219/1494

53. Nardelli, V., D'Amico, V., Casamassima, F., Gesualdo, G., Li, D., Marchesiello, W. M. V., Nardiello, D., Quinto, M. (2019). Development of a screening analytical method for the determination of non-dioxin-like polychlorinated biphenyls in chicken eggs by gaschromatography and electron capture detection. In Food Additives & Contaminants: Part A (Vol. 36, Issue 9, pp. 1393–1403). Taylor & Francis. https://doi.org/10.1080/19440049.2019.1627002

54. DSTU IEC 61619, 2019. Insulation liquids. Contamination by polychlorinated biphenyls (PCBs). Method of determination by capillary column gas chromatography (IEC 61619:1997, IDT).

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