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Analysis of surfactant content in surface water of the Kórnik Commune

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ABSTRACT

Surfactants are chemical compounds with an amphiphilic structure that, due to the presence of hydrophilic and hydrophobic components, exhibit the ability to reduce surface tension and adsorb at phase boundaries, which determines their wide application and analytical significance in environmental research. This paper presents a characterization of surface-active compounds, including their chemical structure, classification based on the structure of the hydrophobic component, basic physicochemical properties, analytical methods used for their determination, range of applications and production volume, and their impact on the aquatic environment. The study area, located in the Kórnik Commune, within the Kórnik-Zaniemyśl channel, was also characterized. Anionic and nonionic surfactant content was determined in surface water samples collected between June and November 2025 from six sites: Lake Bnińskie, the Głuszynka River between the lakes, Lake Kórnickie, and the Skrzyneckie Lakes. Anionic surfactants were determined using the simplified MBAS spectrophotometric method, while nonionic surfactants were analyzed using the BiAS-thio method, a modification of the classic BiAS method based on complex formation with Dragendorff's reagent. The reliability of the analytical procedures used was confirmed by testing environmental samples with the added standard and assessing its recovery.

Keywords: surface water, surfactants, MBAS method, BiAS-thio method.

INTRODUCTION

Surfactants (surface-active compounds) are widely used due to their amphiphilic molecular structure, which translates into their ability to lower surface tension. Therefore, they are used both in households (e.g., detergents) and in industries (e.g., emulsifiers, lubricants, and dispersants). Thanks to their specific structure, they can adsorb onto interfacial surfaces and lower surface tension by reducing the work required to expand the phase boundary. These properties enable the formation of foam, emulsions, and microemulsions, among other things. Unfortunately, they also have a negative impact on water and soil quality. The wide range of applications of this group of compounds poses a risk of their release into the environment as pollutants, which may be caused by uncontrolled sewage discharges and leaky or outdated treatment systems. This paper addresses analytical issues related to monitoring the content of anionic and nonionic surfactants in surface waters.

Surfactants are composed of two structurally and functionally different parts:

- hydrophobic (non-polar),
- hydrophilic (polar).

This combination gives the surfactant molecule an amphiphilic character, which determines its ability to adsorb at phase boundaries and lower surface tension (Rosen, 2004). The amphiphilicity of surfactants is the basis of their action in both technological systems and analytical applications. The hydrophilic (oleophobic) moiety is polar and exhibits an affinity for polar solvents, particularly water. It can have an ionic or nonionic structure, and its chemical structure is highly diverse. The most common hydrophilic groups include carboxylate, sulfate, phosphate, and sulfone moieties. The presence of the hydrophilic moiety determines the surfactant's solubility in water, while its ionic nature determines the classification of the surfactant based on its dissociation behavior in an aqueous environment. The hydrophobic (oleophilic) moiety is nonpolar and exhibits an affinity for nonpolar solvents, such as mineral oils or chloroform. The most common hydrophobic groups are aliphatic or branched alkyl chains and alkylaryl structures. More specific hydrophobic groups, such as fluoroalkyl and silicoalkyl groups, are also known (Kosswig, 2005). The structure of the hydrophobic portion significantly influences the physicochemical properties of a surfactant, including its solubility, ability to form micelles, and adsorption at the phase boundary. The length of the hydrophobic chain is crucial for the surfactant's behavior in solution. An elongated alkyl chain leads to a decrease in water solubility and an increase in solubility in organic solvents, as well as an increased tendency to form micelles and liquid crystal structures. Simultaneously, the melting point of both the surfactant itself and the adsorption film formed at the phase boundary increases. The degree of branching and the presence of unsaturated bonds in the hydrophobic portion result in a lower melting point and improved solubility compared to saturated aliphatic compounds. At the same time, reduced thermal stability and biodegradability are observed, and in the case of unsaturated compounds, oxidation processes leading to the formation of colored forms are possible. The presence of aromatic rings increases surfactant adsorption on polar surfaces, but also reduces their biodegradability and ability to pack at the phase boundary. A special group consists of surfactants containing polyoxypropylene and polyoxyethylene groups. The presence of polyoxypropylene groups increases hydrophobicity and adsorption on polar surfaces, while polyoxyethylene groups increase the hydrophilicity of the molecule. Surfactants containing perfluoroalkyl or polysiloxane groups, in turn, enable very low surface tension values, with perfluoroalkyl surfaces exhibiting both hydrophobic and oleophobic properties (Wyrwas, 2012).

There are many criteria for classifying surface-active compounds, including their application, raw material origin, biodegradability, and chemical structure (Tadros, 2005). The most common and most important classification from the perspective of physicochemical properties is based on the nature of the hydrophilic moiety. Based on the way they dissociate in an aqueous environment, surfactants are divided into nonionic and ionic surfactants, the latter including anionic, cationic, and amphoteric (zwitterionic) surfactants (Farn, 2006).

Anionic surfactants, also known as anionic surfactants, constitute the largest and most common group of surfactants. Their hydrophilic portion is an anionic, providing excellent cleaning and foaming properties. This group includes fatty acid salts (soaps), linear alkylbenzene sulfonates, and fatty acid sulfate esters. These compounds are characterized by good effectiveness, resistance to water hardness, and wide application in industry and households (Cornell University, 2025). Cationic surfactants have a positively charged hydrophilic portion, which favors their adsorption on negatively charged solid surfaces. As a result, they exhibit good wetting and emulsifying properties. The most important group consists of quaternary ammonium salts, including compounds with biocidal properties, such as benzalkonium chlorides, as well as higher primary amines and their salts (Huszla et al., 2018). Amphoteric (zwitterionic) surfactants contain both anionic and cationic groups in their hydrophilic portion. Their properties depend largely on the pH of the environment and the position of the isoelectric point. Above this point, they behave like anionic surfactants, below it like cationic surfactants, while at the isoelectric point, they exhibit characteristics similar to nonionic surfactants. Due to this pH dependence, they have limited industrial significance, but they are used in dermatological and cosmetic products.

Nonionic surfactants are characterized by the lack of a formal electric charge in their hydrophilic portion, the polarity of which results from the presence of strongly electronegative atoms, most often oxygen. The most important representatives of this group include fatty alcohol and alkylphenol oxyethylates, as well as natural surfactants such as saponins. Nonionic surfactants are characterized by a low critical micellar concentration, good biodegradability, and the ability to precisely design their properties by regulating the number of oxyethylene units. This makes them widely used in chemical analysis, industry, and consumer products (Zieliński, 2017). A group of compounds that is gaining increasing importance are biosurfactants, which are metabolites of microorganisms such as bacteria and fungi. Their valuable properties include excellent biodegradability, or even non-biodegradability, compared to conventional surfactants, which minimizes contamination of groundwater and soil. Biosurfactants, as molecules of biological origin, are degraded by microorganisms found in soil. A number of biosurfactants can be distinguished. Glycolipids – the most common biosurfactants, e.g., rhamnolipids, sophorolipids, and mannosylglycolipids. They are produced by bacteria and yeasts. Lipoproteins and lipopolysaccharides – complex compounds containing a lipid and a protein or polysaccharide, e.g., surfactants produced by bacteria of the genus Bacillus. Phospholipids – biosurfactants containing phospholipids, which are components of cell membranes. Polysaccharides – some polysaccharides also exhibit surface-active properties. Neutral lipids – less common, but can also exhibit surfactant properties. Biosurfactants are used in many areas. The petroleum industry – used for bioremediation and removal of petroleum-derived contaminants. The cosmetics and pharmaceutical industries – as ingredients in skincare products, antibacterial agents, and medications. Agriculture – improving nutrient absorption and plant protection. The food industry – as emulsifiers and texture-improving agents. Medicine – potential applications in the treatment of infections and supporting therapy (Dywicki et al., 2020).

PHYSICOCHEMICAL PROPERTIES OF SURFACTANTS

The properties of surface-active compounds result directly from their amphiphilic structure and ability to adsorb at phase boundaries. A key characteristic of surfactants is their ability to reduce surface and interfacial tension, which determines their behavior in aqueous solutions and influences a number of phenomena used in both technology and analytical chemistry. The most important properties of surfactants include: reducing surface tension, the ability to form micelles, foaming, detergency, modifying surface wettability, and emulsification.

Lowering surface tension

In low-concentration solutions, surfactant molecules preferentially adsorb at the water–air or water–solid interface. This is due to the system's tendency to minimize contact between the hydrophobic part of the molecule and the aqueous phase. The presence of surfactant at the interface leads to a weakening of intermolecular water interactions, particularly hydrogen bonds, which reduces the work required to increase the interfacial surface area. Consequently, a decrease in the surface free energy, or surface tension, of the solution is observed (Butt et al., 2006).

Micelle formation

As the surfactant concentration in the solution increases, the interfacial surface gradually becomes saturated. After reaching a certain concentration, called the critical micellar concentration (CMC), further surfactant addition no longer causes significant changes in surface tension. Excess surfactant molecules then self-organize within the solution, leading to the formation of micelles. Micelles are ordered aggregates in which the hydrophobic portions of the molecules are directed inward, while the hydrophilic portions remain in contact with water. The ability to form micelles is crucial in analytics, including micellar liquid chromatography and micellar extraction (Butt et al., 2006).

Foaming

Surfactant foaming involves stabilizing gas bubbles in a liquid. Surfactant molecules adsorb at the gas-liquid interface, orienting their hydrophobic portions toward the gas phase and their hydrophilic portions toward the solution. The resulting liquid film, stabilized by the surfactant layer, limits bubble coalescence and slows down the bubble collapse process. This phenomenon has both technological and analytical implications, as excessive foaming can interfere with some analytical procedures (Butt et al., 2006).

Detergent

Detergency involves the removal of hydrophobic contaminants from solid surfaces. This mechanism is similar to the process of micelle formation, with the difference that hydrophobic surfactant fragments interact with dirt particles, forming aggregates around them stabilized by hydrophilic groups directed toward the aqueous phase. As a result, contaminants are detached from the surface and transferred into solution. The phenomenon of detergency is important, among other things, in sample preparation for chemical analysis (Butt et al., 2006).

Change in surface wettability

Adsorption of surfactants on solid surfaces leads to a modification of their wetting properties. The nature of this change depends on the orientation of the surfactant molecule on the surface. If the hydrophobic portion is adsorbed and the hydrophilic group remains outward, the surface wettability by water increases. In the case of adsorption of the hydrophilic portion, typical for some cationic surfactants, the hydrophobic portion remains outward, leading to a decrease in wettability (Butt et al., 2006).

Emulsification

The ability to emulsify results from the amphiphilic nature of surfactants and their adsorption at the water-oil interface. Surfactant molecules stabilize fine droplets of one phase dispersed in the other, forming a protective layer that prevents their coalescence. In oil-in-water emulsions, the outer layer of the droplets is hydrophilic, allowing them to remain permanently dispersed in the aqueous phase. A similar mechanism occurs in water-in-oil emulsions. The emulsification phenomenon finds applications in sample preparation, extraction, and separation techniques, among others (Butt et al., 2006).

SURFACTANT PRODUCTION IN THE WORLD AND IN POLAND

The use of surfactants is widespread and has been growing steadily since the 1980s. Industrial development, intensive urbanization, increased demand for care products, tightening sanitary requirements, rising civilization standards, and even the simple commercialization of a temporary trend are driving the growing demand for ever-increasing surfactant production. In Poland, surfactant production increased from approximately 40.000 tons to over 320.000 tons annually between 2000 and 2024, representing an eight-fold increase in production over a quarter of a century. Surfactant production intensified after 2004, following

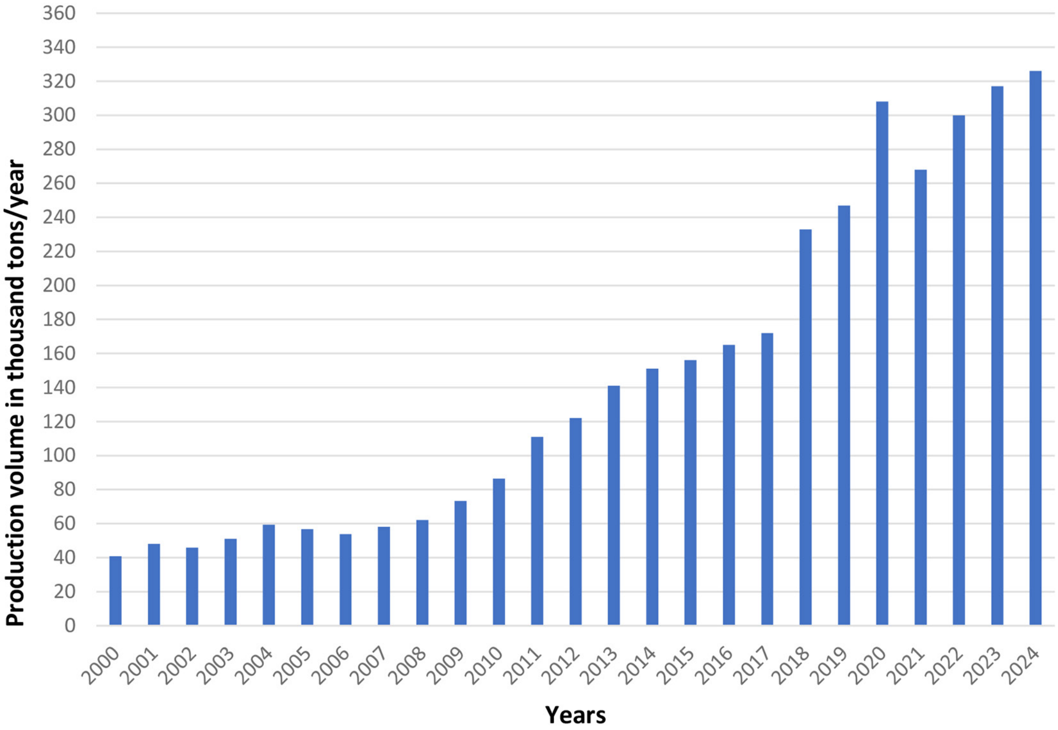

Figure 1. Production of surfactants, including soap and agents used as soap in Poland in 2000–2024 (Central Statistical Office, 2020)

Poland's accession to the European Union (Figure 1) (Central Statistical Office, 2020).

Analyzing data on surfactant production worldwide, it is impossible not to notice that, just like in Poland, production is growing dynamically. According to data from 2023, the global surfactant market was valued at $43 billion, and is expected to reach $62 billion by 2030, with the surfactant market growing at an average of 5% annually (Central Statistical Office, 2020; Grand View Research, 2026).

IMPACT OF SURFACTANTS ON THE ENVIRONMENT

The impact of surface-active compounds (POCs) on the natural environment stems from both their toxicological properties and their characteristic physicochemical characteristics, particularly their ability to reduce surface and interfacial tension. The presence of surfactants in surface waters and wastewater disrupts natural self-purification processes, which constitutes a significant environmental problem. The most significant negative effects of the presence of POCs in the aquatic environment include increased oxygen deficit, accelerated eutrophication processes, the formation of persistent foam on water surfaces, and reduced activity or complete disappearance of aquatic microorganisms. The surface activity of surfactants also promotes the solubilization of hydrophobic compounds, which under normal conditions have very low solubility in water. This applies to pesticides and other persistent organic pollutants, among others, whose bioavailability and mobility in the environment significantly increase. Toxicological studies conducted on aquatic organisms such as bacteria and algae have demonstrated a clear negative impact of surfactants on the metabolic processes and growth of these organisms. The toxicity of surfactants is strongly dependent on their chemical structure, with particularly adverse effects observed in compounds containing aromatic rings. Some surfactants have the ability to penetrate fish skin or accumulate in the organisms through food, leading to their bioaccumulation and biomagnification in the food chain. Consequently, these compounds can also affect the human body, for example, by inhibiting the activity of selected enzymes. Surfactants also exhibit irritating and damaging effects on the skin. For a long time, nonionic surfactants were considered relatively safe, but recent research indicates that even poly(ethylene glycol) ethers, generally considered harmless, can have an adverse effect on skin cells. The impact of surfactants on the functioning of biological wastewater treatment plants is also a significant problem. Even relatively low surfactant concentrations, exceeding 20 mg/L, negatively impact activated sludge microorganisms. Higher concentrations disrupt the structure of the sludge flocs and significantly reduce its biological activity. This phenomenon is particularly important in the case of industrial wastewater, where surfactant concentrations can reach values of 1 g/L or higher (Schmitt, 2001).

METHODS OF ANALYSIS OF SURFACE-ACTIVE COMPOUNDS

The analysis of surfactants is an essential element in the quality control of water, wastewater, and industrial products. Due to the diverse chemical structure of surfactants and their physicochemical properties, numerous analytical methods have been developed, varying in their scope of application, sensitivity, and selectivity.

Titration methods

Titrimetric methods are among the classic techniques for quantitative surfactant determination. Currently, they are used less frequently, primarily due to the development of modern instrumental methods, but they are still used in routine analyses. Anionic surfactants are determined using, among other methods, two-phase titration using cationic titrants, such as Hyamina 1622, in the presence of mixed indicators (dimidium bromide–disulfone blue). Alternatively, other cationic surfactants and color indicators, such as bromophenol blue or methylene blue, are used. Acid-base methods after reaction with p-toluidine hydrochloride and potentiometric determination of olefin sulfates in non-aqueous media are also used. Cationic surfactants are most often determined by two-phase titration using anionic surfactants or by complexometric methods with sodium tetraphenylborate in the presence of a suitable color indicator. In the case of non-ionic surfactants, potentiometric titration using molybdophosphoric acid is used (Alfa Chemistry, 2025).

Electrochemical methods

Electrochemical methods, particularly tensometric analysis, are used to analyze surfactants, especially nonionic surfactants. This technique is based on measuring the capacitive current associated with the adsorption of surfactant molecules on the electrode surface. The content of the analyzed compound is determined based on changes in the intensity of an amperometric peak, e.g., ethyl acetate, in the presence of the surfactant. Electrochemical methods are often used in conjunction with BiAS, which allows for increased sensitivity and selectivity of the determinations (Wyrwas, 2012; Wyrwas et al., 1998).

Spectrophotometric methods

Spectrophotometric methods currently constitute one of the most important groups of analytical techniques used for surfactant determination. Their popularity stems from high accuracy, relatively low reagent consumption, and the ability to determine very low analyte concentrations. The MBAS method is commonly used for determining anionic surfactants, while the BiAS method using Dragendorff's reagent is used for determining oxyethylates. Cationic surfactants are determined by the Kunkel method, based on the formation of ion pairs between the surfactant molecule and disulfone blue. After extraction of the ion pair into the chloroform phase, its quantity is determined spectrophotometrically after appropriate sample preparation by measuring absorbance at a wavelength of 628 nm (Wyrwas, 2012; Wyrwas and Zgoła-Grześkowiak, 2014b).

Chromatographic methods

Thin-layer chromatography (TLC) is primarily used for the qualitative analysis of mixtures of anionic and nonionic surfactants. This method is simple and inexpensive, but has limited accuracy and requires considerable analytical experience. High-performance liquid chromatography (HPLC) is primarily used for the quantitative analysis of individual surfactants, although it can also be used as an auxiliary method in qualitative analysis. Gas chromatography (GC) is rarely used due to the low volatility of surfactants and is usually limited to pyrolysis chromatography (Liu et al., 2009; Shimadzu Corporation, 2018).

SURFACE WATER MONITORING IN POLAND

Monitoring by the Chief Inspectorate for Environmental Protection (GIOŚ) indicates that surfactants are subject to some testing as part of surface water quality assessments. However, this type of pollutant is relatively rarely subject to broader analysis, particularly when it comes to nonionic surfactants, which are currently becoming the dominant surfactant group in production. This stems from the complexity of the analysis, which includes hundreds of compounds with surface-active properties. Instrumental methods are not very well suited to handle such a complex matrix. Extractive-spectrophotometric methods are available, which allow for the determination of the sum of surface-active compounds of a given type. In reports from monitoring rivers and reservoirs, surfactant concentrations show significant seasonal and spatial variability, with higher values during periods of intense sewage runoff and rainfall. In some studies, surfactant concentrations in rivers fluctuate around 0.1–2 mg/L, while in lakes they were usually lower, often below 0.5 mg/L. Contaminated river waters, on the other hand, can reach as high as 1.0–5 mg/L. Such high concentrations occur near large agglomerations and industrial plants (Institute of Meteorology and Water Management – National Research Institute, 2020; Makała et al., 2023; Solipiwko-Pieścik and Wolska, 2024; Szymańska et al., 2025; Szymański et al., 2001).

RESEARCH METHODOLOGY

Water samples were collected from June to November at six sampling points along the Głuszynka River and its associated reservoirs. The sampling points were located from south to north and included the following locations (Figure 2):

1. Lake Bnińskie on the Szyja Peninsula.
2. The Głuszynka River between Lake Bnińskie and Lake Kórnickie near the mouth of Lake Kórnickie.
3. Lake Kórnickie at the promenade.
4. The Głuszynka River between Lake Kórnickie and Lake Skrzyneckie Duże near the Daglezja hotel.
5. Lake Skrzyneckie Duże.
6. Skrzyneckie Małe on the beach from the side of the village of Skrzynki.

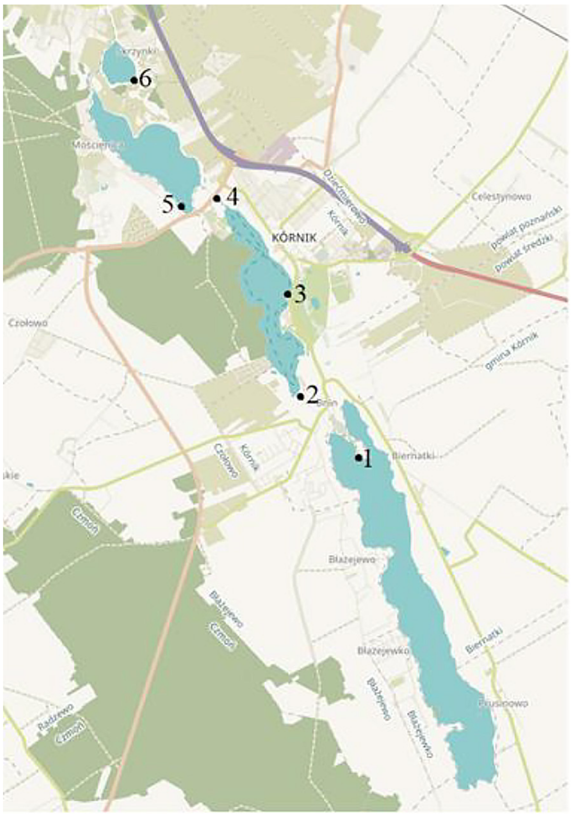

Figure 2. Sampling location

Determination of anionic surfactants in surface waters using the simplified MBAS method

Principle of marking

The content of anionic surfactants in surface waters was determined using the simplified MBAS (Methylene Blue Active Substances) method. This method belongs to the group of extraction-spectrophotometric techniques and is commonly used in water and wastewater analysis (Polish Committee for Standardization, 2002). The principle of the method involves the formation of an ion pair between the positively charged methylene blue cation and the anion of a surfactant. The resulting ion pair is hydrophobic, which allows for its selective extraction into the organic phase. Chloroform is used as the extractant, into which the complex is transferred, retaining its characteristic blue color. The color intensity of the organic phase is proportional to the concentration of anionic surfactants present in the analyzed sample. It should be noted that soaps, due to the relatively low molecular polarity and weaker interactions with methylene blue, are not determined with high accuracy using this method (Jones and Esposito, 2000). The absorbance maximum of the formed complex occurs at a wavelength of 652 nm (Jurado Alameda et al., 2006). The classic version of the MBAS method involves initial alkalization of the sample, addition of a neutral methylene blue solution, triple extraction with chloroform, and re-extraction with an acidic dye solution. The detection limit for this method is approximately 0.1 mg/L (Wyrwas and Zgoła-Grześkowiak, 2014a). Due to the considerable labor intensity of the procedure and the high consumption of chloroform, a simplified version was developed. The simplified MBAS method was modified to reduce the number of reagents used, particularly the toxic and expensive chloroform. Surface-active sulfonate anions exhibit a strong affinity for methylene blue cations, causing a significant portion of the complexes to transfer to the organic phase during the first extraction. Therefore, the simplified version of the procedure uses a single extraction step (Namieśnik and Konieczka, 2007). In the first stage of analysis, water samples were filtered through filter paper to remove suspended solids. To the resulting filtrate, 5 mL of acidic methylene blue solution was added, followed by extraction with 10 mL of chloroform for 3 minutes. After phase separation, the organic layer was transferred to centrifuge tubes and centrifuged for 2 minutes to further separate the phases. The aqueous layer was discarded as waste, while the chloroform layer was subjected to additional filtration. Absorbance of the extract was measured at a wavelength of 652 nm against chloroform as a reference. A blank sample, prepared analogously using deionized water, was performed for each series of determinations, allowing for control of reagent purity and the accuracy.of the analytical procedure.

Calibration curve of the simplified MBAS method

To generate a calibration curve, a series of seven tests were performed on samples with known sodium dodecylbenzenesulfonate concentrations. A specific amount of the standard was added to 200 mL of deionized water, and the analytical procedure for the simplified MBAS method was followed. Table 1 presents the relationship between absorbance and the amount of DBSNa (sodium dodecylbenzenesulfonate) standard.

Figure 3 shows the calibration curve of the simplified MBAS method for DBSNa in the range of 0÷0.1 mg.

Table 1. Dependence of absorbance on the amount of DBSNa standard in the simplified MBAS method

Amount of standard added [mg]	Absorbance
0.000	0.06461
0.005	0.08926
0.010	0.20045
0.025	0.44255
0.050	0.73744
0.075	1.18371
0.100	1.65449

Based on the obtained linear regression formula (1), a formula for determining concentration based on absorbance was developed. The coefficient of determination R^2 was 0.9971.

$$A = 16.14 \cdot X \tag{1}$$

$$X = \frac{A}{16.14} \tag{2}$$

where: A – absorbance, X – analyte content [mg in sample].

Precision, detection limit and quantification limit of the simplified MBAS method

To determine the precision of the conducted tests, the analysis of a standard sample containing 0.025 mg of the analyte was repeated seven times. Table 2 presents the precision of the simplified MBAS method for 0.025 mg of DBSNa.

The detection limit is the smallest quantity or concentration of a substance that can be detected using a selected analytical method with a specified probability. It is determined using the formula (Sawyer et al., 2003):

$$LOD = X_{mean} + 3 \cdot SD \tag{3}$$

where: LOD – detection limit, X_{mean} – mean blank value, SD – standard deviation.

The limit of quantification defines the minimum amount or concentration of a substance that will allow its content to be quantified with a specified accuracy and precision. It is determined using the formula [29]:

$$LOQ = 3 \cdot LOD \tag{4}$$

where: LOQ – detection limit, LOD – detection limit.

The detection and quantification limits of the method were determined based on blank samples and the results are summarized in Table 3.

Determination of non-ionic surfactants by the BiAS-thio method

Principle of marking

The iodobismuthate method for determining oxyethylates with a final absorbance measurement of the bismuth–thiourea complex (BiAS-thio) was used to determine nonionic surfactants. This method is an advanced modification of the classic BiAS (Bismuth Active Substances) method. The standard version of the BiAS method is characterized by low sensitivity, limited precision, and significant reagent consumption, making it unsuitable

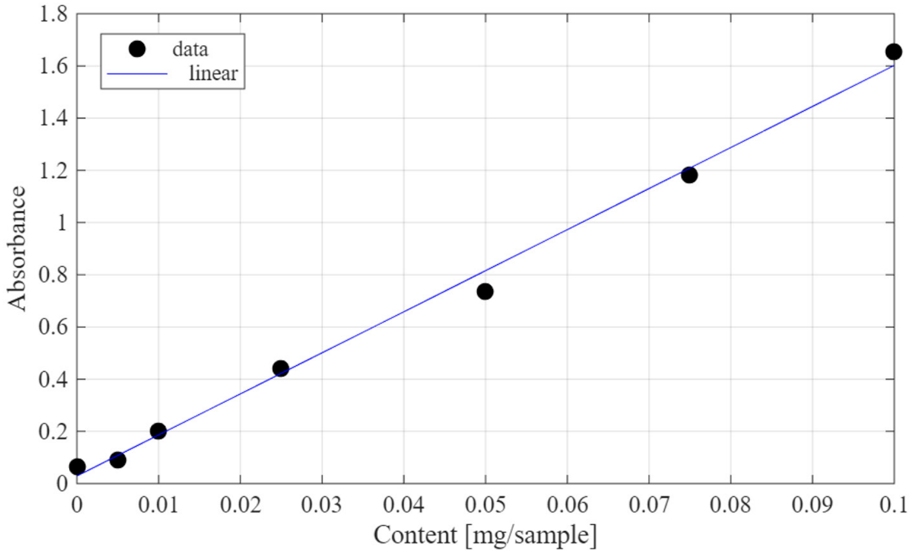

Figure 3. Calibration curve of the simplified MBAS method for DBSNa in the range of 0–0.1 mg

for routine analysis of nonionic surfactants in surface waters (Myers, 2012). The BiAS-thio method is based on the reaction of nonionic surfactants with Dragendorff's reagent in the presence of a reducing agent, leading to the formation of sparingly soluble ion pairs containing iodobismuthates. In the next step, the resulting precipitate is dissolved in an acidified thiourea solution, resulting in the formation of a colored bismuth–thiourea complex. This complex absorbs electromagnetic radiation in the visible light range, with an absorbance maximum at 468 nm. In the classic BiAS method, separate solutions were used to dissolve the ion pair precipitate and to complex bismuth ions. In the BiAS-thio method, these functions are performed by a single reagent – an acidified thiourea solution – which significantly simplifies the complex analytical procedure and improves its accuracy and repeatability. Due to the low concentrations of nonionic surfactants found in surface waters, analysis was preceded by a sample concentration step using solid-phase extraction (SPE). The surfactants were adsorbed onto SPE columns and then eluted with 10 mL of methanol. The eluate was evaporated at 70 °C until dry. To the prepared sample, 1 mL of Dragendorff's reagent was added, and after ion pair precipitation, the suspension was transferred to centrifuge tubes and centrifuged for 5 minutes at 12.000 rpm. After centrifugation, the sediment was washed three times with 1 mL of glacial acetic acid to remove excess unbound iodobismuthates. Then, 2 mL of thiourea solution in HNO_3 was added to the remaining sediment, obtaining a yellow solution of the bismuth-thiourea complex. Absorbance was measured at a wavelength of 468 nm against deionized water as a reference (Wyrwas, 2012).

Table 2. Precision of the simplified MBAS method for 0.025 mg DBSNa

Sample No.	Absorbance	Content [mg in sample]
1	0.45255	0.0269
2	0.37130	0.0232
3	0.36598	0.0230
4	0.42875	0.0268
5	0.35203	0.0215
6	0.35637	0.0223
7	0.38237	0.0238
Mean	-	0.0239
SD	-	0.0022
RSD	-	9.28%

Calibration curve of the BiAS-tio method

To generate a calibration curve, a series of eight tests were performed for samples with known Triton X-100 concentrations. A specific amount of the standard was added to 200 mL of deionized water, and then the analytical procedure for the BiAS-thio method was followed. Table 4 presents the relationship between absorbance and the amount of Triton X-100 standard.

Figure 4 shows the calibration curve of the BiAS-tio method for TX-100 in the range of 0÷0.125 mg.

Based on the obtained linear regression formula (5) (the coefficient of determination R^2 was 0.9977), a formula for determining concentration based on absorbance was developed.

$$A = 12.93 \cdot X \tag{5}$$

$$X = \frac{A}{12.93} \tag{6}$$

where: A – absorbance, X – analyte content [mg in sample].

Table 3. Calculation of the detection limit and the quantification limit of the simplified MBAS method

Blank number	Absorbance	Blank value [mg]
1	0.03987	0.0023
2	0.04518	0.0026
3	0.04734	0.0024
4	0.04752	0.0028
5	0.05187	0.0030
6	0.05405	0.0035
7	0.06462	0.0041
Mean	-	0.0029
SD	-	0.0005
LOD	-	0.0046
LOQ	-	0.0137

Table 4. Dependence of absorbance on the amount of Triton X-100 standard

Amount of standard added [mg]	Absorbance
0.000	0.01294
0.005	0.04785
0.010	0.12097
0.025	0.31324
0.050	0.60868
0.075	0.94416
0.100	1.22995
0.125	1.69916

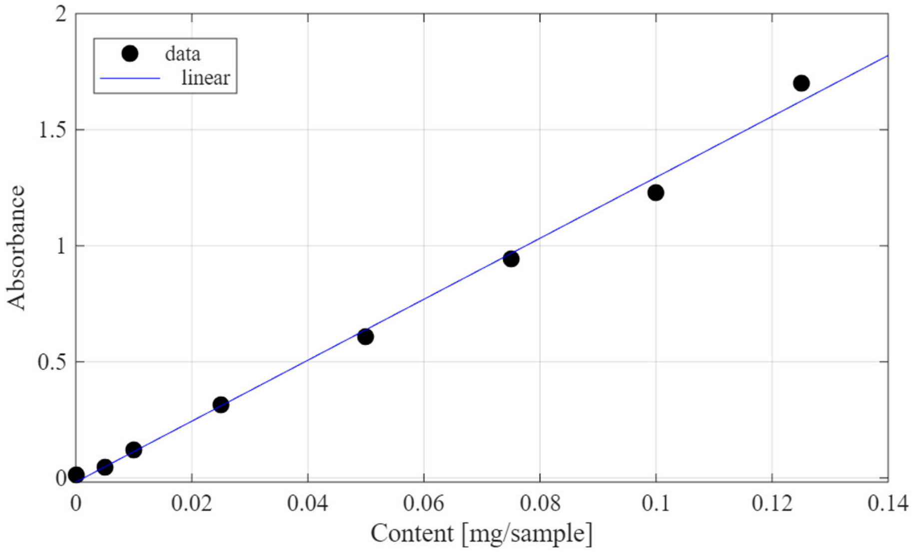

Figure 4. Calibration curve of the BiAS-tio method for TX-100 in the range of 0÷0.125 mg

Precision, detection limit and quantification limit of the BiAS-tio method

To determine the precision of the conducted tests, the analysis of a standard sample containing 0.025 mg of the analyte was repeated six times. Table 5 presents the precision of the BiAS-thio method determinations for 0.025 mg of TX-100.

The detection and quantification limits were determined in a manner analogous to the MBAS method based on blank samples, and the results are presented in Table 6.

Table 7 presents a summary of the lowest and highest concentrations of anionic surfactants, and Table 8 presents a summary of the lowest and highest concentrations of non-ionic surfactants.

The highest mean concentrations of anionic surfactants were observed in Lake Kórnickie and amounted to 0.120 mg/L. Similar values (0.118 mg/L) were observed in the Głuszynka River at the outlet of Lake Kórnickie. A high mean concentration was also observed in Lake Skrzyneckie Małe and amounted to 0.098 mg/L. The remaining points had comparable mean concentrations in the range 0.061-0.069 mg/L. The highest maximum concentrations were observed at the same points as the highest mean concentrations. They were 0.178 mg/L for Lake Kórnickie in October and 0.180 mg/L for the Głuszynka River at its outlet in November. All anionic surfactant concentration values are lower than those measured in the Głuszynka River during the last measurements in 2006.

The highest average concentrations of nonionic surfactants were observed in Lake Skrzyneckie Duże in October and Lake Skrzyneckie Małe in August, reaching 0.361 mg/L and 0.357 mg/L, respectively. The concentration of nonionic surfactants was also high in the Głuszynka River at the

Table 5. Precision of BiAS-tio method determinations for 0.025 mg TX-100

Sample No.	Absorbance	Content [mg in sample]
1	0.30103	0.0235
2	0.35447	0.0273
3	0.30114	0.0234
4	0.27268	0.0212
5	0.30897	0.0240
6	0.36643	0.0288
Mean	-	0.0212
SD	-	00028
RSD	-	11.25%

Table 6. Determination of the detection limit and quantification limit of the BiAS-tio method

Blank number	Absorbance	Blank value [mg]
1	0.00862	0.00068
2	0.01295	0.00102
3	0.01517	0.00116
4	0.01526	0.00114
5	0.01399	0.00109
6	0.01405	0.00107
Mean	-	0.00102
SD	-	0.00019
LOD	-	0.0016
LOQ	-	0.0048

Table 7. Summary of the average, lowest, and highest observed anionic surfactant concentrations

No.	Reservoir	Average [mg/L]	Maximum [mg/L]	Minimum [mg/L]
1	Lake Bnin	0.070	0.082	0.054
2	Głuszynka 1	0.067	0.098	0.048
3	Lake Kórnik	0.125	0.179	0.071
4	Głuszynka 2	0.119	0.181	0.076
5	Lake Skrzyneckie Duże	0.060	0.103	0.044
6	Lake Skrzyneckie Małe	0.095	0.130	0.065

Table 8. Summary of the average, lowest, and highest observed concentrations of nonionic surfactants

No.	Reservoir	Average [mg/L]	Maximum [mg/L]	Minimum [mg/L]
1	Lake Bnin	0.043	0.074	0.017
2	Głuszynka 1	0.040	0.051	0.033
3	Lake Kórnik	0.060	0.074	0.046
4	Głuszynka 2	0.271	0.353	0.172
5	Lake Skrzyneckie Duże	0.362	0.483	0.244
6	Lake Skrzyneckie Małe	0.356	0.468	0.244

Table 9. Summary of the average content of anionic and nonionic surfactants in the tested surface waters

No.	Reservoir	Average content of anionic surfactants [mg/L]	Average content of non-ionic surfactants [mg/L]
1	Lake Bnin	0.070	0.043
2	Głuszynka 1	0.066	0.040
3	Lake Kórnik	0.121	0.060
4	Głuszynka 2	0.119	0.271
5	Lake Skrzyneckie Duże	0.063	0.360
6	Lake Skrzyneckie Małe	0.097	0.356
7	Warta	0.051	0.061

outlet of Lake Kórnickie, reaching 0.270 mg/L. Concentrations in other bodies of water are several times lower. The lowest concentration was observed in the Głuszynka River at the outlet of Lake Bnińskie (0.039 mg/L). Table 9 summarizes the average anionic and nonionic surfactant concentrations in the tested surface waters.

CONCLUSIONS

Based on the conducted studies, it was found that the surface waters of the Kórnik Commune meet the criteria for Class I purity in terms of surfactant content, as defined by the Regulation of the Minister of Environmental Protection, Natural Resources and Forestry of November 5, 1991, with limit values for this class being below 0.2 mg/L for anionic surfactants and 0.5 mg/L for non-ionic surfactants. The highest concentrations of anionic surfactants, close to the limit values, were recorded in Lake Kórnickie and in the Głuszynka River at its outlet, while the two Skrzyneckie Lakes were most polluted with non-ionic surfactants. Comparison of the obtained results with literature data indicates that the concentrations of anionic surfactants in the studied water bodies are lower than the values determined in the Głuszynka River in 2005 and 2006. However, for Lake Kórnickie and the Głuszynka at its outlet, they are higher than the concentrations recorded in 2004, indicating variability in anthropogenic pressure over time. Of particular note is the significant increase in the content of nonionic surfactants at the outlet of Lake Kórnickie compared to its inlet and the middle section, indicating the existence of a local pollution source between the sampling points. In this case, uncontrolled discharges of industrial wastewater are highly likely, as this area overlaps with the urban development of Kórnik. Concentrations of anionic and nonionic surfactants in the surface waters of the Kórnik Commune were also found to be higher than in the Warta River in Poznań, despite Poznań being a much larger urban center. This may indicate greater effectiveness in protecting the Warta's water quality, stemming from its role as a drinking water source, extensive sewerage network, and systematic modernization of wastewater treatment plants. However, within the Kórnik Commune, there is a risk of uncontrolled sewage discharges from unsewered buildings and insufficient efficiency of local treatment plants. Analysis of the structure of the pollutants studied revealed comparable anionic and nonionic surfactant contents, with the nonionic surfactant fraction becoming dominant in the final sections of the flow-through basins. This confirms the shift in production trends observed in recent years toward nonionic surfactants and the consequences of their biodegradation, leading to the formation of poly(ethylene glycols), which are relatively difficult to degrade. The results obtained for the content of anionic and nonionic surfactants in the waters of the Kórnik Commune vary depending on the sampling location. For logistical reasons, samples were not collected simultaneously at all six sampling points. The studied body of water is subject to dynamic changes related to surface water flow, rainfall, seasonal changes, and temperature changes. Different types of surfactants and their degradation products also undergo different biodegradation rates. In summary, potential sources of surfactants entering the surface waters of the Kórnik Commune include:

- transport and communication – vehicle emissions, fuel, oil, and street-polluting spills. During rainfall, they are washed directly into surface waters, often bypassing storm sewers.
- surface runoff from agricultural fields – containing fertilizers, herbicides, pesticides, and surfactants,
- release of poorly treated sewage from domestic sewage treatment plants,
- illegal landfills and dumps,
- uncontrolled discharge of untreated sewage directly into the environment.

The effectiveness and suitability of the analytical methods used were confirmed by validation. Both the simplified MBAS method and the BiAS-tio method, modifications of classical methods, enabled lower detection and quantification limits and improved precision, which is crucial in surface water analysis. The detection and quantification limits for the MBAS method were 0.0046 mg/L and 0.0137 mg/L, respectively, while for the BiAS-tio method they were 0.0016 mg/L and 0.0048 mg/L. The precision of the determinations, determined for a concentration of 0.025 mg/L, was 9.28% for the MBAS method and 11.25% for the BiAS-tio method. Additionally, the effectiveness of the methods was confirmed by tests with the addition of a standard, in which the recovery for the MBAS method was close to 100%, while for the BiAS-tio method it was approximately 70%, which should be attributed to the multi-stage nature of the analytical procedure and possible losses of the analyte during its implementation.

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