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Determination of Bisphenol A (BPA) in the Port of Gdynia Waters Using Gas Chromatography Coupled with Mass Spectrometry (GC-MS)

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Abstract: This paper presents a procedure for the determination of bisphenol A (BPA) in seawater. Gas chromatography coupled with mass spectrometry (GC-MS) was used as the analytical method, preceded by analyte isolation via solid-phase extraction (SPE). Initially, the best conditions for extraction, derivatization, and GC-MS analysis were established. The need for derivatization in the determination of BPA was investigated, and for this reason, two methods of sample preparation were compared: with and without the derivatization step. The parameters of the two methods of sample preparation were compared with each other, and a more efficient method was chosen for the analysis of marine water samples. Afterwards, the validation process was carried out and the following parameters were determined: limit of detection (LOD), limit of quantification (LOQ), linearity, precision, reproducibility, and repeatability. Finally, the results of the determination of bisphenol A in water samples collected from five harbor basins of the Port of Gdynia using an unmanned mobile research unit, HydroDron-1, were presented. The identified concentrations ranged from 0.01 µg/L to 0.03 µg/L, depending on the investigated area.

Keywords: bisphenol A; surface port waters; Port of Gdynia; GC-MS(SIM); SPE

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1. Introduction

Bisphenol A (BPA) is an organic compound that has been widely used in the industry. It was first synthesized in 1891 by the chemist A. Dianin. This compound is formed during the process of reaction of phenol with acetone under the conditions of high temperature and low pH, with the participation of catalysts [1]. It has a characteristic faint smell of phenol and exists in the form of crystals or flakes. Often, products containing BPA are heat- and pressure-resistant. This is the reason why they are used as protective layers in electrical applications, the building industry, and the electronics industry [2].

BPA is massively used in the manufacture of reusable plastics. Most of the items containing BPA are used in daily life, for example, potable water bottles, cans, plastic containers, or food packaging [3]. Some of the BPA containers may be in constant contact with food. BPA can potentially affect human health through consumption, along with its presence in food and drinks [4]. For several years, there has been an ongoing discussion about BPA's influence on the hormonal system and the need to eliminate the use of packages containing this substance [5,6]. There is a growing body of data confirming its possible endocrine-disrupting activity [7]. BPA can have far-reaching physiological effects through disrupting hormone signaling. Invertebrates and vertebrates in early developmental periods are the most sensitive to BPA toxicity [8]. Also, the immune system of aquatic organisms can be adversely affected by environmental pollutants. BPA, which has been

shown to be non-toxic or safe at low levels, can become highly toxic when combined with other marine pollutants, such as heavy metals, and has genotoxic and cytotoxic activity. A study conducted by Di Paola et al. in 2021 presents that BPA, together with cadmium and chromium, could cause an acute inflammatory response in zebrafish larvae [9].

Although scientists in the mid-1930s noted the first reports of the embryotoxic and teratogenic effects of BPA, it is only in the last few years that this compound has received extensive attention [10,11]. Due to its negative impact on human health, more countries are introducing bans or restrictions on the use of BPA [12]. Pollutants that exist in water have an impact on the surrounding environment and human health; therefore, it is necessary to test the quality of water and determine the presence of pollutants [13]. Canada was the first country in the world to officially recognize BPA as a toxic and dangerous substance to humans and the environment. Canada also introduced legal regulations, despite numerous protests from the Canadian and American chemical industry. Increasingly, appropriate legal regulations are reducing the possible scope of BPA applications [14]. In the EU directive (2011/8/EU), the use of BPA has been banned, albeit only in infant feeding bottles [15]. Several EU member states have implemented national bans on the use of BPA in selected products. For example, France has stopped the production, export, and import of any food packaging containing BPA [16], while Japan has banned the use of BPA in the production of thermal receipt papers [17]. In Polish legislation, BPA control in the environment is not currently required.

In the European arena, there are no legal regulations for BPA monitoring in the aquatic environment. Despite the fact that BPA is quickly degraded by bacteria under aerobic conditions, the commonness of reusable plastic products and accompanying BPA production leads to BPA accumulation in the environment [18]. Although numerous articles have raised the issue of the presence of BPA in surface water [19], drinking water [20], and wastewater [21], BPA has not been included in the US or European priority pollutant lists [22]. In the risk assessment of compounds that are dangerous to humans, education about their presence and fate in the environment is a significant aspect [23]. There is a high probability that BPA will become an obligatory monitoring parameter for the aquatic environment in the next few years. Currently, BPA is mentioned only in Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption.

There are limited studies that investigated the presence of BPA and its concentration in seawater. Therefore, the authors of this study analyzed water samples from the Port of Gdynia to determine the content of BPA in seawater and to expand the knowledge on this topic.

This study presents an analytical method for the determination of BPA content in surface and bottom seawater using solid phase extraction (SPE) and gas chromatography (GC) coupled with mass spectrometry (MS) and selected ion monitoring (SIM). In the literature, two methods of BPA analysis are reported—the chromatographic determination of BPA in an unchanged form or its derivative BPA-di-TMS. In order to optimize the research method, the authors developed two methods of sample preparation and verified them. The first method included the derivatization stage, whereas the second one skipped this process. On the basis of the obtained results, the first method was selected as the more efficient one. For this method, a validation process was carried out, which was then used for the analysis of samples taken from the basins of the Port of Gdynia.

2. Materials and Methods

2.1. Study Area

The Port of Gdynia is located in the southern part of the Baltic Sea on the western coast of the Gulf of Gdansk. The total area of the port is 7.55 km^2 [24]. The Port of Gdynia is secured by breakwater of a 2.5 km length. As a result, the water in the harbor is not freely exchanged with Baltic Sea water. The primary source of pollution in port seawater is the large-scale industrial and commercial activity from the city and port operations [25]. The

Port of Gdynia consists of two areas, the West Port (inner port) and the East Port (outer port) [26]. The distributions of pollutants in the two areas of the Port of Gdynia differ from each other. The East Port is an area strictly linked to land and human impact (Basins V–VIII), while in the West Port, the exchange of water is significant (Basins I–IV) [27]. Our studies were carried out in selected harbor basins located in both of the mentioned areas. The locations of the sampling stations are presented on the map (Figure 1).

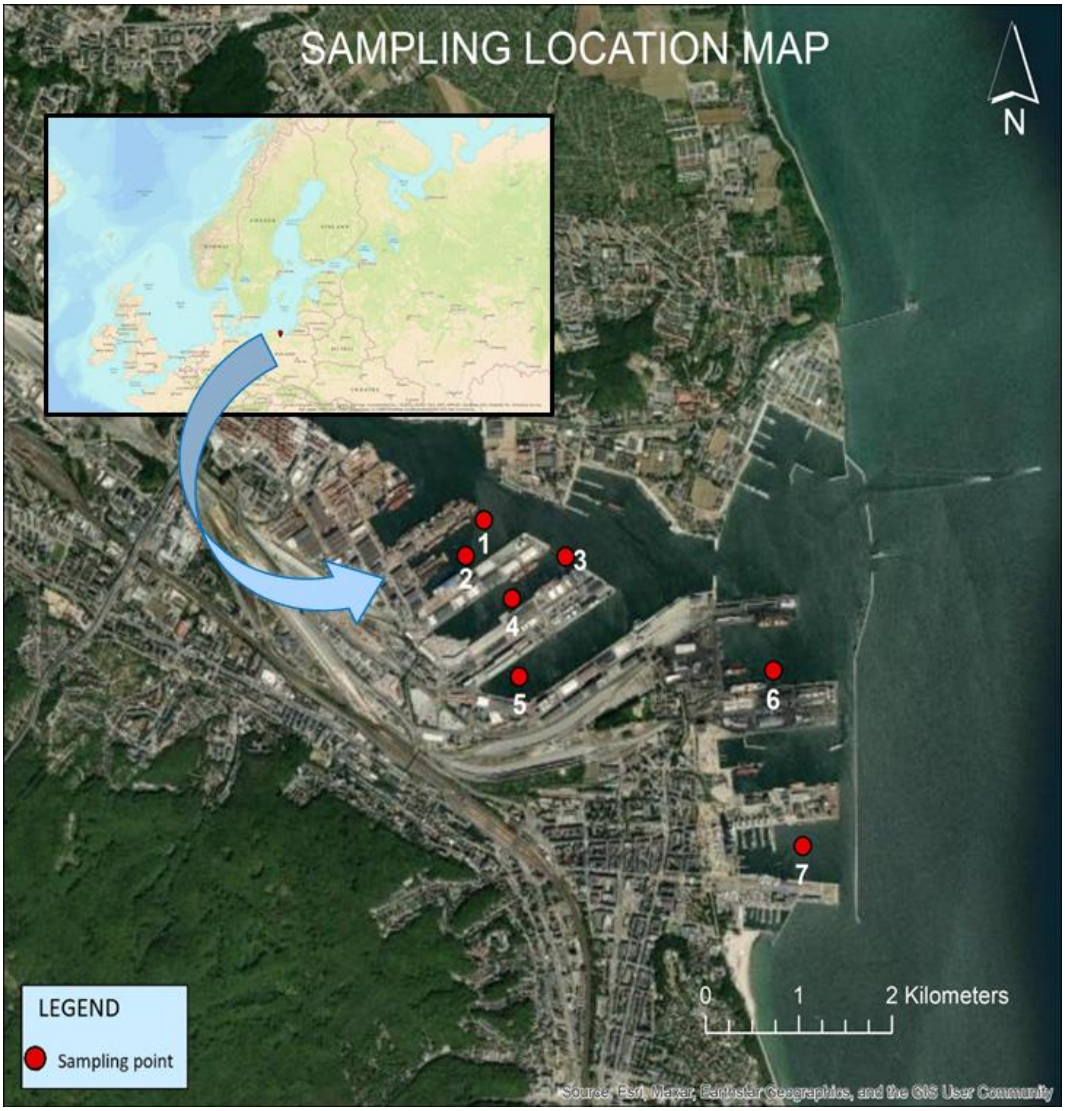


Figure 1. Seawater sampling location—Port of Gdynia (No. 1–7) harbor basins—site map.

2.2. Port Water Sampling

Water samples were collected in four measurement campaigns that took place during the four seasons of 2022 (Winter campaign: 28 February–3 March; Spring campaign: 16–19 May; Summer campaign: 18–21 July; Autumn: 17–20 October 2022). The dates of sampling campaigns throughout the year were determined based on historical studies of the water purity of the harbor basins from 2012–2019 [28]. During each of the measurement campaigns, samples from up to two sampling points were taken per day. Seawater samples were taken with a bathometer in accordance with ISO 5667-9:1992. During all four water sampling campaigns, the weather conditions in the Port of Gdynia were favorable, with a wind force of 1–2 on the Beaufort scale and a calm sea.

Surface and bottom water samples were collected from five harbor basins in the Port of Gdynia. Sampling points were selected after taking into account various factors

such as the analysis of historical results from the surveyed region, availability and depth. Harbor basins are areas of limited maneuverability due to their small size. The use of a small unmanned unit can be the solution for such areas. Sampling with the HydroDron-1 (Figure 2a) may be carried out in autonomous or remote-control mode. In this particular project, the remote-control mode was used. Using two NISKIN-type bathometers (volume 7.5 L) (Figure 2b) attached to HydroDron-1, water samples were collected, transferred into glass bottles directly after sampling and transported to the laboratory. The concentration of Bisphenol A was determined in the collected samples. The analysis took place at the Environment Protection Laboratory of Maritime Institute, Gdynia Maritime University (PCA Certificate No. AB 646).



(**a**) (**b**)

Figure 2. (**a**) HydroDron-1 vessels in the Port of Gdynia harbor basin [29] (photo, A. Bojke); (**b**) the moment of transferring water into glass bottles from the bathometer (photo, A. Bojke).

2.3. Chemicals/Reagents

The standard of Bisphenol A used to prepare standard solutions and spiking solutions for the validation process was from AccuStandard (Catalog No: M-1626-01S). As the internal standard, BPA-d16 from CPAchem (Catalog No: 962-87-6) was used. The derivation reagent was N,O-bis(trimethylsilyl)trifluoroacetamide with trimethylchlorosilane BSTFA:TMCS (99:1) from Sigma-Aldrich (product no: 15238). For the extraction stage, Bakerbond Octadecyl (C18) cartridges from J.T.Baker were used. Hexane, methanol and acetone with purity for analysis and dichloromethane with purity for gas chromatography (MS) were from Merck (Germany).

2.4. Apparatus

The Multi-Blok Heater (LabLine, Instruments, Dubuque, IA, USA) was used to heat samples during the derivatization step. For solid-phase extraction (SPE), the vacuum manifold J.T.Baker (SPE 12-G; prod. no. 7520-94) was used. The concentration of BPA was quantified using gas chromatograph 7890A GC fitted with HP 7693 Autosampler, interfaced with mass spectrometer 5977A MSD with an EI of 70 eV as the ionization source (Agilent Technologies, Santa Clara, CA, USA).

2.5. Sample Preparation

SPE extraction is the method generally used for the determination of BPA in water [30,31]. The usage of several types of extraction cartridges for BPA determination can be found in the literature, for example, Strata-X from Phenomenex [2,22], Strata C-18 E from Phenomenex [15], Oasis HLB from Waters [17] and BondElute-PPL from Varian [3]. In this study, Bakerbond Octadecyl-C18 (500 mg) cartridges from J.T.Baker were used.

The water sample (1000 mL) previously acidified to pH 1.8–2.2 with HCl was spiked with 100 µL of BPA-d16 (0.5 µg/mL) as an internal standard. The cartridges were conditioned sequentially with 6 mL of acetone, 6 mL of methanol and 6 mL of demineralized water using a vacuum manifold. After conditioning with methanol, it is important that the cartridges do not dry out. The water sample was connected to the SPE and passed through the cartridge at a flow rate of 3–4 drops/sec. The cartridges were then dried in a nitrogen atmosphere for 30 min. Theanalytes were eluted from the cartridges with 10 mL of acetone. The extract was evaporated to dryness and the precipitate was dissolved in 1 mL of hexane. At this stage, one of two solutions was used; either the extract was subjected to derivatization followed by GC-MS chromatographic analysis (Method 1), or the non-derivatized extract was analyzed (Method 2). The scheme of the procedures is presented in Figure 3.

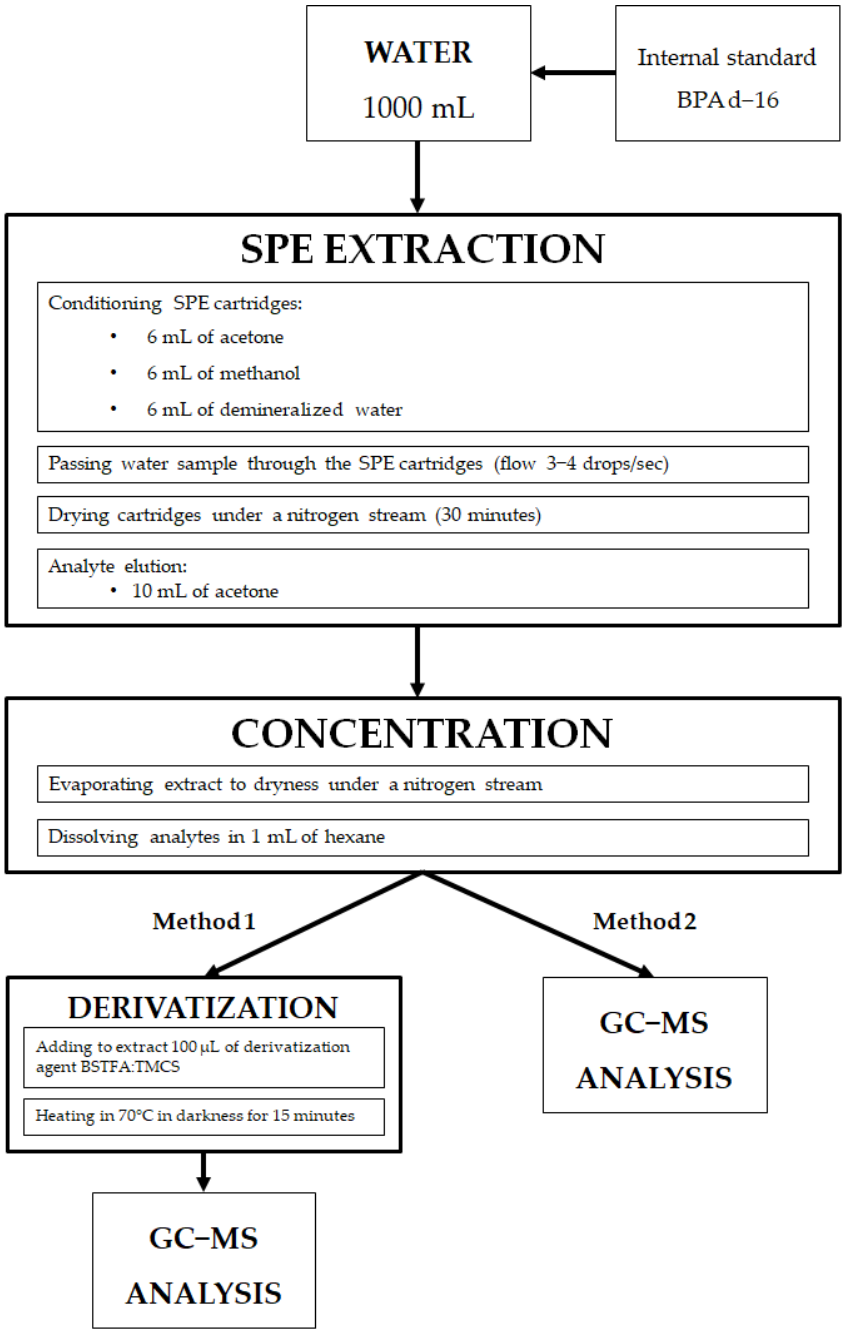


Figure 3. Sample handling scheme.

2.6. Derivatization

As the derivatization agent, a mixture of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) with trimethylchlorosilane (TMCS) was used. According to the manufacturer's information, BSTFA takes part in the reaction as a substrate, while TMCS is a catalyst. In this reaction, hydrogen groups are replaced by an alkylsilyl group which increases the compounds' volatility. Additionally, derivatization enhances the thermal stability and non-polarity of the compounds. The scheme of reaction of BPA with BSTFA is shown in Figure 4. For derivatization, 100 µL of BSTFA:TMCS was added to 1 mL of the sample extract and then kept in the dark at 70 °C for 15 min. After cooling to room temperature, the samples were analyzed via GC-MS.

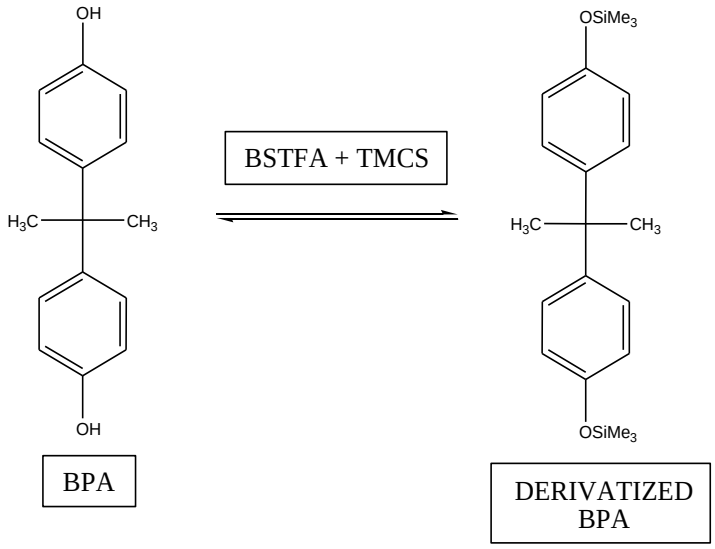


Figure 4. Scheme of reaction of bisphenol A (BPA) with N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) in presence of TMCS as catalyst.

2.7. GC Analyse

Gas chromatography coupled with a mass spectrometer was used for the determination of the qualitative and quantitative compounds. An amount of 1 µL of the sample extract was dosed to the injector in the pulsed splitless mode. The column Rxi 5MS (30 m × 0.32 mm × 0.25 µm) was used for separation with helium as a carrier gas. The exact operating parameters of the apparatus are presented in Table 1.

Table 1. GC and MS parameters.

GC and MS Parameters		
Chromatograph model	Agilent Technologies 7890 A	
Detector	Agilent Technologies 5977 A	
Chromatography column	Rxi 5MS (30 m × 0.32 mm × 0.25 µm)	
Dosing system	Pulsed splitless	
Injection volume	1 µL	
Carrier gas	Helium	
Gas flow	1.5 mL/min.	
Temperature program	150 °C → 30 °C/min → 200 °C → 5 °C/min → 250° → 30 °C/min → 300 °C per 7 min	
Injector temperature	300 °C	
Total analysis time	20.3 min	
Detector mode	SIM	
m/*z* ratio	Target ion	Confirmation ion
Derivatized BPA	357	358, 372
Derivatized BPA-d16	368	369, 386
BPA	213	228, 119
BPA-d16	223	241, 113

BPA was identified based on the relative retention time of the standard solution analyzed in the SCAN mode. Knowing the retention time and the m/z ratio, quantification was performed in the SIM mode using the target and confirmation ions (Table 1) (Figures 5 and 6).

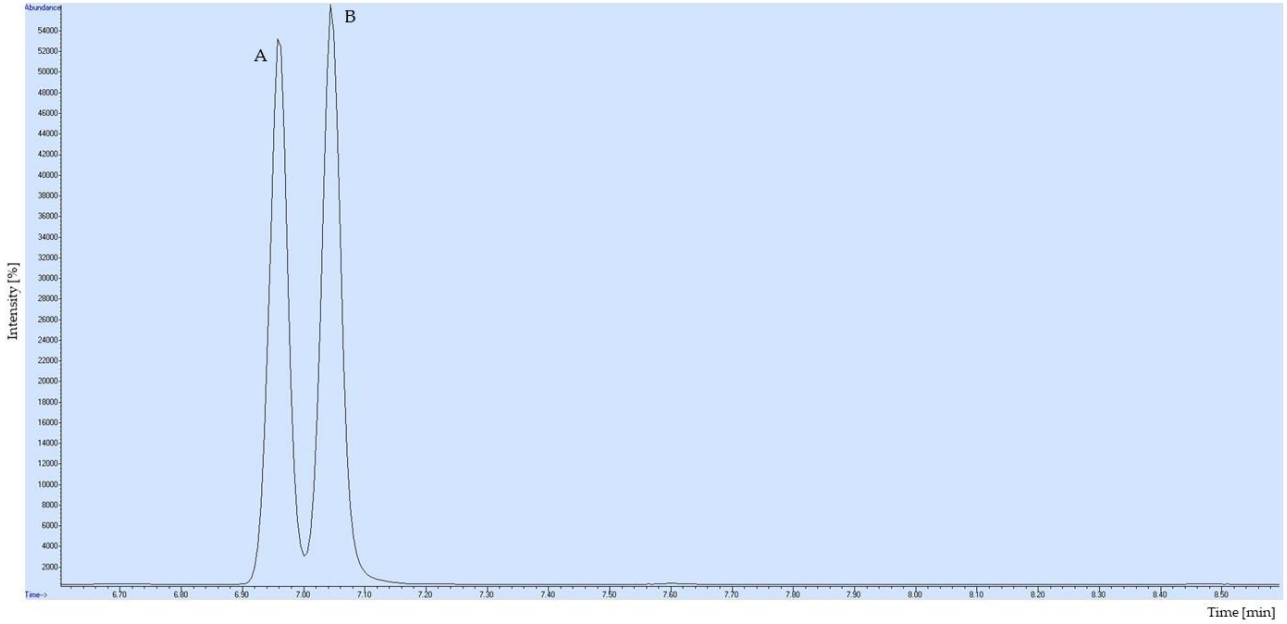


Figure 5. Chromatogram selected ion monitoring mode (SIM) for derivatized BPA-d16 1.0 (µg/mL) (A) and BPA 1.0 (µg/mL) (B).

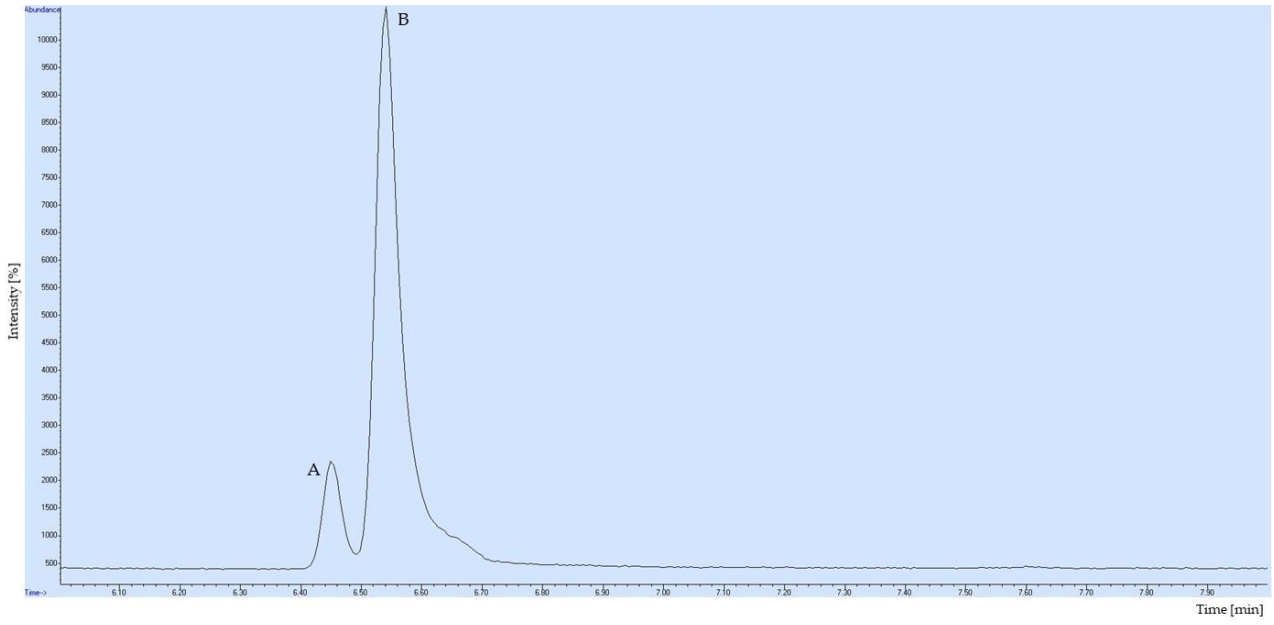


Figure 6. Chromatogram's selected ion monitoring mode (SIM) for non-derivatized BPA-d16 1.0 (µg/mL) (A) and BPA 1.0 (µg/mL) (B).

2.8. Validation Parameters

During the validation process, the following parameters were determined: the limit of detection (LOD), the limit of quantification (LOQ), linearity, recovery, precision, repeatability and reproducibility. The LOD and LOQ were determined based on blank samples, treated in the same way as the water samples, including all reagents and all steps of the analytical procedure. Linearity was checked in the established range, by analyzing the

series of standard solutions in hexane with the internal standard added to the extract and derivatized.

The rest of the validation parameters were determined based on matrix samples. For this purpose, the seawater was spiked with BPA spiking solution to obtain concentrations representing the working range. The added quantities of the BPA standard in seawater were 0.01 µg/L, 0.1 µg/L, 4.0 µg/L and 5.0 µg/L respectively. The initial concentration of the analyte was included in the calculations. A minimum of 6 replicates were prepared for each concentration. Precision was calculated as the relative standard deviation (RSD) expressed as a percentage. Repeatability was determined as the product of the precision and the elemental number of samples in a given concentration. Reproducibility was achieved on the basis of interlaboratory tests.

2.9. Statistical Analysis

Statistical analysis was performed using Past version 4.13. The homogeneity of variance was tested with Levene's test and a normal distribution of data was tested with the Shapiro–Wilk test. Based on the results, further tests were chosen. The occurence of statistically significant differences between the results of samples taken over four seasons was determined via the Kruskal–Wallis test. The groups of results were compared using the post hoc Dunn's multiple comparison test with the Bonferroni adjustment. For results below the LOQ, the value of the LOQ was adopted. The significance was set at $p < 0.05$.

3. Results and Discussion

3.1. Method Preparation

Table 2 presents the basic analytical parameters illustrating the usefulness of the two tested analytical methods. In the Method 1, extracts previously subjected to the derivatization process were analyzed. No derivatization reagent was used in Method 2. The LOD and LOQ of the method were determined based on blank samples. The remaining parameters were calculated on the basis of the results of analysis of two series of water samples with the addition of a standard solution (BPA concentration in water 1 µg/L).

Table 2. Results of comparing the two methods with and without derivatization.

Parameters	Method 1	Method 2
LOD	0.004	0.012
LOQ	0.013	0.037
BPA concentration (µg/L)	1	1
N	7	7
Recovery (%)	95.5	105.76
Precision (%RSD)	2.22	2.95
Repeatability (%)	5.88	7.81

The obtained results show that both methods can be successfully used to determine the presence of BPA in water. Most of the calculated parameters are at a comparable level. A significant difference can be observed only in the LOD and LOQ parameters. The derivatization process allows the obtention of a better detector response. Consequently, a lower concentration of BPA in the water sample can be detected compared to that of non-silylated BPA. Kim et al. [32] have made a summary of BPA determination methods investigated by scientists and it clearly shows that anlysis with derivatization is more frequently used for BPA determination in different kinds of samples.The results of this study are consistent with the literature as they showed that both approaches are correct, but the method with the derivatization step allows the obtention of lower values of the LOD and LOQ. BPA is successfully analyzed via GC-MS after derivatization using several silylating agents, for example, MSTFA [15] or BSTFA [22]. Zafra et al. [21], in his study on GC-MS determination of BPA and its chlorinated derivates in urban wastewater, tested five different

silylation reagents (TMSA, TMSI, BSTFA, TMCS, and the mixture of TMCS:HMDS:pyridine in a ratio of 1:3:9) and chose BSTFA as the most adequate for his research.

On the basis of the obtained results and the literature data, the research method has been established. It includes steps such as extraction on the C18 cartridges and derivatization with BSTFA:TMCS as the silylation agent.

3.2. Validation Parameters

The assessment of the LOD and LOQ is an important validation step. The LOQ, calculated from the LOD, determines the lowest concentration of the analyte in a given matrix which can be determined with appropriate precision and accuracy. For this purpose, blank samples were used to evaluate the limit of detection. The concentration of BPA in the blank samples ranges from 0.0006 to 0.0034 µg/L. The LOD was calculated and amounted to 0.004 µg/L. The LOQ is defined as the value of three LODs and is equal to 0.013 µg/L (Table 2). Due to these results, the concentration of 0.01 µg/L was adopted as the limit of quantification. Linearity has been demonstrated in the ranges of 0.01–0.30 µg/mL and 0.30–5.0 µg/mL (Figures 7 and 8) and the regression coefficients were 0.99943 and 0.99921 respectively. These values are similar to the values mentioned in the literature [15,16]. The quantification range was established at 0.01–5.0 µg/mL.

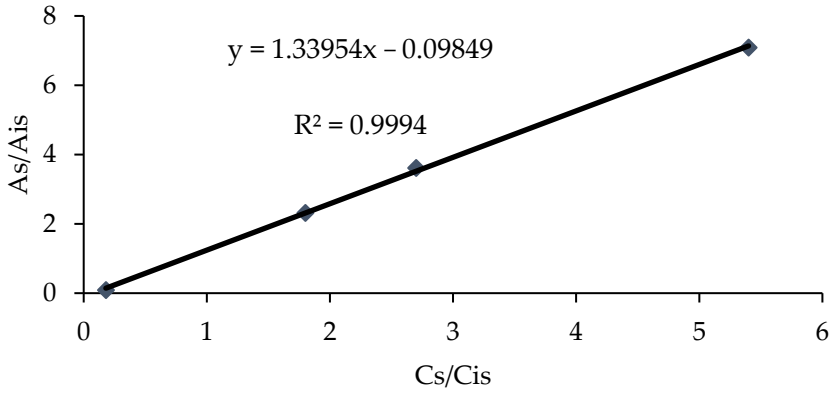


Figure 7. BPA calibration curve for the range of 0.01–0.30 µg/mL (As—peak area of BPA standard; Ais—peak area of BPA-d16 internal standard; Cs—concentration of BPA standard (µg/mL); Cis—concentration of BPA-d16 internal standard (µg/mL)).

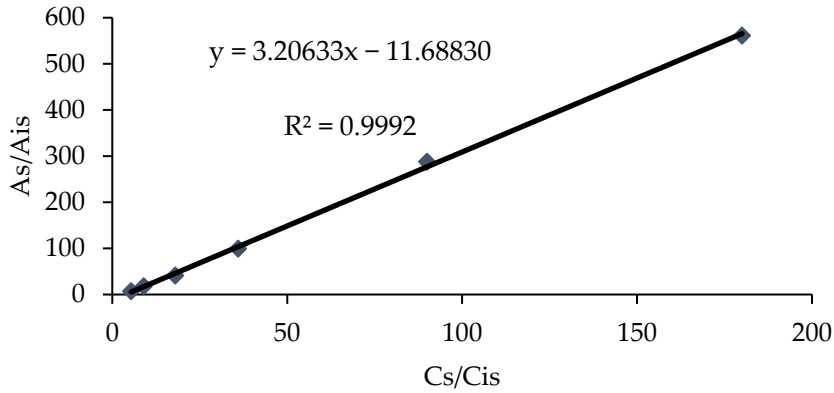


Figure 8. BPA calibration curve for the range of 0.30–5.0 µg/mL (As—peak area of BPA standard; Ais—peak area of BPA-d16 internal standard; Cs—concentration of BPA standard (µg/mL); Cis—concentration of BPA-d16 internal standard (µg/mL)).

The recovery for different concentrations of BPA in seawater is in the range of 82.94–101.67% (Table 3). Montagner [22] in his work obtained a recovery of 91–113% and Selvaraj [15] reports a recovery of 93.9% (±2.0) for surface water. Wang [33] reported that a satisfactory BPA recovery efficiency is 104.2–113.5%.

Table 3. Values of recovery, precision and repeatability of BPA analysis via SPE-GC/MS(SIM) method.

BPA Concentration (µg/L)	n	Recovery (%)	Precision (%)	Repeatability (%)
0.010	10	92.00	4.35	13.75
0.100	6	101.67	5.55	13.60
4.000	8	82.94	6.72	19.01
5.000	7	92.42	2.84	7.53

The results of precision and repeatability are presented in Table 3. The analyses were performed at four concentration levels. The precision did not exceed 7%, which is a correct result—the literature data recommend a precision value below 20% [34]. Repeatability was calculated on the basis of precision and was within 7–20%. Cunha et al. [35] obtained similar values for validation parameters, such as linearity, recovery and precision for BPA in their studies. Reproducibility was calculated on the basis of proficiency testing and was 4.63%, which is an acceptable result. The laboratory's ability to measure BPA in water has been verified by participating in Aquacheck AQ 606-34D proficiency testing organized by LGC Standards. The obtained Z-score indicator was −0.11, which is a satisfactory result.

The validation parameters obtained in this work are consistent with the values presented in the literature for the same method of BPA analysis. However, there are other methods used by scientists which allow the detection and quantification of BPA at lower levels of concentration. Performing dispersive liquid–liquid microextraction (DLLME) followed by GC-MS detection allowed scientists to determine the LOD value for BPA at the level of 0.46 pg/mL and the LOQ value at the level of 1.52 pg/mL [36]. Another technique used for the determination of BPA is that of using the Raman spectrometer which is capable of detecting BPA in a concentration equal to 0.1 pg/mL [37]. In the case of the determination of BPA via liquid-phase microextraction (LPME) followed by GC-MS analysis, the LOD and LOQ values were similar to those obtained using SPE-GC/MS technique and were 0.014 and 0.024 µg/L respectively [38].

3.3. BPA Concentration in Port of Gdynia

A total number of 56 samples were analyzed using the SPE-GC/MS method. The statistical analysis showed that statistically significant differences existed between the summer and winter results and between the summer and autumn results (Table 4).

Table 4. The *p* values of Dunn's multiple comparison test with the Bonferroni adjustment for results of BPA concentration in samples of seawater taken over four seasons.

	Winter	Spring	Summer	Autumn
Winter		1.000	0.014	1.000
Spring	1.000		0.088	1.000
Summer	0.014	0.088		0.014
Autumn	1.000	1.000	0.014	

The detected concentrations of BPA in water samples from Port of Gdynia ranged from 0.01 µg/L to 0.03 µg/L or were below the LOQ (Table 5). The total BPA residue level in the seawater of Port of Gdynia was the highest in the summer. The increase in the concentration of BPA in the summer may be associated with the increased movement of ships and boats and the greater activity of people at the seaside. It was confirmed that temperature is one of the main factors influencing BPA's migration [39]. Other studies proved that higher temperatures influence BPA release but to very low degree [36]. This is consistent with our results as a minimal increase in the concentration of BPA could be seen in the summer. Curiously, BPA was not detected above the LOQ in any of the bottom samples in winter and only two surface samples showed quantifiable amounts of BPA. The number of microplastics in the water is not correlated with the location of the harbor basins [27]. This is consistent with our results because the concentrations of BPA in all

basins of Port in Gdynia were at a similar level. As there are no legal regulations on the BPA concentration in surface water, the obtained results were compared with the PNEC values (predicted no-effect concentration). They were set by HELCOM in 2010 at level of 150 ng/L for surface water [40]. Wright-Walters et al. [41] have shown that adverse effects on the aquatic environment can occur between concentrations of 0.0483 µg/L and 2280 µg/L. Other researchers tested the BPA concentrations in water samples from the Gulf of Gdansk in 2011–2012. The concentrations of BPA ranged from 20.8 to 124.4 ng/L in samples of the surface water layer collected near the Port of Gdynia. The near-bottom surface concentration ranged from 6.2 to 67.3 ng/L [40]. Those values are comparable with values obtained in this study.

Table 5. The concentration of BPA in seawater samples from the Port of Gdynia.

Basins of the Port of Gdynia	Location No.	Concentration (µg/L)			
		Winter		Spring	
		Surface	Bottom	Surface	Bottom
Basin No. VI	1	<0.01	<0.01	0.010 ± 0.003	0.010 ± 0.003
	2	0.010 ± 0.003	<0.01	0.02 ± 0.01	0.010 ± 0.003
Basin No. V	3	0.010 ± 0.003	<0.01	<0.01	0.010 ± 0.003
	4	<0.01	<0.01	0.010 ± 0.003	0.010 ± 0.003
Basin No. IV	5	<0.01	<0.01	0.010 ± 0.003	0.010 ± 0.003
Basin No. I	6	<0.01	<0.01	<0.01	<0.01
Basin No. III	7	<0.01	<0.01	<0.01	0.010 ± 0.003
		Summer		Autumn	
		surface	bottom	surface	bottom
Basin No. VI	1	0.010 ± 0.003	0.010 ± 0.003	0.010 ± 0.003	0.010 ± 0.003
	2	0.010 ± 0.003	0.010 ± 0.003	<0.01	0.010 ± 0.003
Basin No. V	3	0.02 ± 0.01	0.010 ± 0.003	<0.01	0.010 ± 0.003
	4	0.02 ± 0.01	0.010 ± 0.003	0.010 ± 0.003	0.010 ± 0.003
Basin No. IV	5	0.03 ± 0.01	0.02 ± 0.01	0.010 ± 0.003	0.010 ± 0.003
Basin No. I	6	0.02 ± 0.01	0.010 ± 0.003	0.010 ± 0.003	0.010 ± 0.003
Basin No. III	7	0.010 ± 0.003	0.010 ± 0.003	<0.01	0.010 ± 0.003

Among the data reported by Ribeiro et al. [42] for water in the Mondego estuary in Portugal and by Cunha et al. [35] for water in the estuaries of the Tagus and Douro rivers, the highest level of BPAs was detected in autumn and winter. The maximum concentration detected in our study (0,03 µg/L) was lower than the concentration values of samples collected from the coastal environments (Straits of Singapore) near six major wastewater treatment plants [38]. The presence of BPA was also investigated in surface water samples from the Beibu Gulf, South China Sea. The results showed that BPA was in the water samples with levels ranging from 5.26 to 12.04 ng/L [43]. The highest noted BPA concentration in the Port Dickson was 59.01 ng/L [44]. The levels of BPA in the Kaveri, Vellar and Tamiraparani rivers, India, were in the range of 2.8–136 ng/L [15]. In other studies, European rivers were tested and the reported level of BPA was much higher, i.e., up to 2970 ng/L in Spain and 776 ng/L in Germany [45,46]. Studies conducted in Poland showed a concentration of BPA in the range of 23.5–132.2 ng/L in the outlet of the longest Polish river—the Vistula in Swibno [40]. Compared to those in results from all over the word, the concentrations of BPA in samples from Port of Gdynia were relatively low.

4. Conclusions

The exposure of the aquatic environment to emerging pollutants is a global problem that is particularly important in many seas due to the impact of anthropogenic activities. The aim of the study was to evaluate the content of BPA in seawater samples collected in one year in Port of Gdynia. In order to carry this out, an attempt to optimize BPA analysis in

surface water was made. The studies showed that using the SPE-GC/MS method, BPA can be analyzed both in the derivatized form and the non-changed form, but that a lower LOQ can be achieved for analysis using derivatization agent BSTFA. The values of all validation parameters were consistent with those in the literature reports. This study provided reliable and detailed data to assess the degree of BPA contamination in Port of Gdynia and showed that the concentration of BPA in seawater is very low.

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