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Determination of volatile organic pollutants in water samples of White Drin River, Kosovo

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Abstract

In this paper, the concentrations of some volatile organic compounds (VOC) in water samples from the White Drin River (Kosovo) are presented. The White Drin River is one of the largest river in Kosovo and one of the largest in the Balkans. Water of the river could be affected by anthropogenic pollutions that comes mainly by directly discharges of urban wastewaters. The volatile organic pollutants that were analyzed were chlorobenzenes (mono-, di-, tri-, tetra-, penta- and hexachlororbenzene) and BTEX (Benzene, Toluene, Ethylbenzene, ortho-, meta- and para-Xylenes). Water samples were taken in February 2023, at 15 different stations from Drini Waterfall (near Peja to Albanian border). The head space solid phase micro-extraction (HS/SPME) method was used for the extraction and quantitative analysis of chlorobenzenes and BTEX followed by gas chromatography (GC) techniques. This method presents advantages for the analysis of volatile pollutants because it eliminates the use of organic solvents and different sample treatment steps that often lead to erroneous results. The sensitivity and reproducibility of HS is favorable for volatile organic pollutants. The adsorption of organic pollutants was carried out on a polydimethyl siloxane (PS) fiber at a temperature of 50°C for 30 minutes. Desorption process was carried out in the injector of the gas chromatograph at high temperature (250°C for 10 seconds). The qualitative and quantitative analysis of chlorobenzenes (mono-, di-, three-, tetra-, penta- and hexachlorobenzene) was realized in the GC/ECD apparatus, while the analysis of BTEX was carried out in the GC/FID apparatus. VOC were present almost in all analyzed samples. BTEX presence is related to the high intensity of transport near the river. The presence of chlorobenzenes can be a consequence of urban spills, of cleaning/sanitization processes, as degradation products of other compounds (pesticides, PCBs, etc.).

Introduction

Head-space (HS) technique is commonly used mainly for the concentration (extraction) and analysis of volatile organic compounds. In this technique the sample first establishes a balance between the gas phase (above in the head-space) and the sample which may be liquid or solid. This balance is established using moderate temperatures (30 - 70°C) to create the opportunity for volatile compounds to pass into the gas phase. After that, a polymer fiber which has high adsorption capabilities (Solid Phase Micro-Extraction or SPME) is used to fix homogeneous gas sample and pass it directly to the injector of the gas chromatograph (GC). The injector carries out the passage of the sample from the polymer fiber to the column of the apparatus through the desorption process at high temperature (220 - 280°C). Chromatographic columns enable the separation of all volatile compounds found in the sample. The head-space technique can be used in static and/or dynamic mode, Today, HS technique is fully automated. The advantage of HS technique is operation without the use of solvents and in a single step the extraction and analysis of the sample compounds is performed [1-2]. HS/SPME analysis followed by GC analysis consists of two steps: Adsorption of the compound from the sample and transfer of the sample directly to the gas

chromatograph by desorption process. The amount of analyte transferred to the instrument is proportional to the volume of the gas phase, and to the concentration of the analyte, accepting that the space above the sample is in equilibrium with the sample [3, 4].

Material and Method

Water sampling in Drini i Bardhe River: Water samples were taken in 15 different stations of the White Drin River. Water samples were sampled and analyzed in February 2023. A quantity of 2.5 litre of water from each station in Teflon bottles. The sampling method was based on ISO 5667-3: 2018. Water samples were tranported and conserved at +4°C prior to their analyze.

Analyzes of BTEX in water samples: For the determination of BTEX, 5 ml of water samples were taken from the stations of the White Drin River in SPME bottles with a volume of 10 ml. The bottles were equipped with Teflon stoppers suitable for their analysis by Head-space technique. The manual SPME syringe equipped with a 100 um PDMS (Polydimethyl siloxane) fiber was inserted through the Teflon stopper into the top of the sample. The bottle was placed at a temperature of 50°C for 30 minutes. PDMS fiber was transferred to the gas chromatograph injector where desorption process was carried out at 250°C for 10 seconds. For the qualitative and quantitative determination of BTEX, the Varian GC 450 apparatus equipped with a flame ionization detector (FID) and a PTV injector was used. The separation of BTEX was performed in VF-1ms (30m length x 0.33mm internal diameter x 0.25µm film), suitable for their separation [5-7].

Analyzes of chlorobenzenes in water samples: For the chlorobenzenes analyze, 5 ml of water samples were taken in SPME bottles with a volume of 10 ml. The bottles were equipped with Teflon stoppers suitable for their analysis by Head-space technique. The manual SPME syringe equipped with a 100 um PDMS (Polydimethyl siloxane) fiber was inserted through the Teflon stopper into the top of the sample. The bottle was placed at a temperature of 50°C for 30 minutes. The process of desorption for the chlorobenzenes was realized to the gas chromatograph injector at 260°C for 10 seconds. Qualitative and quantitative determination of chlorobenzenes was realized in a Varian GC 450 apparatus equipped with electron capture detector (ECD). The separation of chlorinated benzene derivates was performed by using a RTX-5 capillary column (30m length x 0.25mm internal diameter x 0.25µm film), suitable for their separation [8, 9].

Results

In this study, water samples from the White Drin River, which is one of the largest river in Kosovo, were analyzed. The water samples were taken in February 2023. The analysis of volatile organic compounds was carried out using the HS/SPME technique followed by gas chromatography technique. The qualitative and quantitative analysis of BTEX was realized by means of GC/FID, while the analysis of chlorobenzenes was realized by means of GC/ECD. The processed data for BTEX and chlorobenzenes in the water of the river are shown in Tables 1 and 2.

Table 1. BTEX data in water samples of White Drin River, February 2023

BTEX	Mean	STDEV	Median	Min	Max
Benzene	0.256	0.052	0.223	N.D.	1.187
Toluene	0.141	0.047	0.135	N.D.	1.583
m-Xylene	0.026	0.011	0.028	N.D.	0.186
p-Xylene	0.105	0.028	0.103	N.D.	0.748
o-Xylene	0.039	0.586	0.038	N.D.	0.102
Ethylbenzene	0.089	0.009	0.086	N.D.	0.211

Table 2. Data of chlorobenzenes in water samples of White Drin River, February 2023

Chlorobenzene	Mean	STDEV	Median	Min	Max
Chlorobenzene	0.428	0.103	0.418	N.D.	2.158
1,2-Dichlorobenzene	0.075	0.026	0.069	N.D.	0.126
1,3-Dichlorobenzene	0.052	0.013	0.055	N.D.	0.284
1,4-Dichlorobenzene	0.036	0.017	0.038	N.D.	0.206
1.3.5-Trichlorobenzene	0.129	0.029	0.131	N.D.	0.245
1.2.3-Trichlorobenzene	0.068	0.016	0.057	N.D.	0.355
1.2.4-Trichlorobenzene	0.227	0.047	0.225	N.D.	0.954
Tetrachlorobenzene	0.124	0.049	0.128	N.D.	0.850
Pentachlorobenzene	0.210	0.058	0.223	N.D.	1.147
Hexaclorbenzene	0.364	0.086	0.354	N.D.	2.352

N.D. – Not Detected or lower than Limit of detection (LOD)

Discussion

BTEX were detected in all analyzed samples. The highest level was found for station near the border to Albania (station 15) and the minimum near Drini Waterfall (station 1). Presence of BTEX in the water of the river could be

related to the automobilist transport, the spilling/accidents of hydrocarbon near the river and beyond, and the impact created by mechanical businesses (car service) in the area of river. Waste from other businesses operating in this area is also not excluded. It was noted presence of Benzene in higher quantities than other volatile compounds. Its presence is a consequence of its identification in high quantity at some stations where there may be some point source of it. This could also be the value of the moment of this compound or spillage of hydrocarbon waste from any vessel. Benzene levels do not exceed the permitted rate for surface waters according to EU 2008/105.

The presence of chlorobenzenes were noted in all analyzed water samples. Their maximum was noted in several stations located near cities or villages while the minimum in waterfall of White Drin station. Their presence may be a consequence of direct discharges of liquid urban waste from houses and/or buisnesses, due to hygiene/cleaning products, as a consequence of the degradation of large organic molecules with chlorine (pesticides, PCBs, etc.) At a higher level were found chlorobenzene, pentachlorobenzene and hexachlorbenzene, whose presence was identified at a higher level at several stations near of urban centers or agricultural areas. The presence of these compounds may be mainly by wastewater discharges or degradation products of pesticides and other molecules. The levels of volatile organic pollutants in the water of the port of Durres were similar to the levels reported in previous works for Balkan area [8-10].

Conclusion

In this study, water samples from the White Drin River, which is one of the largest river in Kosovo, were analyzed. The analysis of chlorobenzenes and BTEX was carried out by HS/SPME technique followed by GC/FID/ECD technique. Volatile organic pollutants were present in almost all analyzed water samples. BTEX presence is related mainly to the intensity of automobilist transport near the river. Spills of hydrocarbon by gas stations, agro-mechanicals or mechanical businesses operating in this area are not excluded. Momentum values and the influence of water flow are not excluded. Benzene was the compound that was most frequently identified in the highest quantity for all samples. Chlorobenzenes were also detected for most of the samples analyzed. Chlorobenzene, pentachlororbenzene and HCB were identified at higher level in several stations of the river. The presence of chlorobenzenes can be a consequence of urban spills, of cleaning/sanitization in houses and businesses, as degradation products of other compounds (pesticides, PCBs, etc). The levels of VOC in the water of White Drin River were similar to the levels reported in previous works for the water of some Albanian rivers. The presence of BTEX and chlorobenzenes in the water samples of the White Drin River shows that the monitoring of this area should be continuous.

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