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Determination of antifreeze substances in the airport runoff waters by solid phase microextraction and gas chromatography-mass spectrometry method

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Abstract

A new method has been developed for the determination of antifreeze agents such as ethylene glycol (EG), propylene glycol (PG) and diethylene glycol (DEG) in the samples of airport runoff water. The method is based on headspace solid-phase microextraction (HS-SPME) of target analytes which is coupled with gas chromatography-mass spectrometry (GC-MS). Until now, there was a lack of appropriate methodology for collecting reliable data about the concentration levels of these toxic de/anti-icing substances in the new type of environmental samples such as the airport runoff water. The evaluation of green extraction technique, i.e. HS-SPME resulted in establishing the optimal extraction conditions, as follows: 85-µm PA fibre coating, extraction temperature of 80 °C, extraction time of 60 min, desorption time of 7 min at 270 °C, addition of 1.5 g of NaCl, and the sample volume of 8 mL. The recovery ranged from 67 to 89%, which demonstrates that the HS-SPME technique is a powerful method for extracting antifreeze agents from the airport stormwater samples. The developed HS-SPME–GC/MS methodology allowed for the rapid, sensitive, precise and accurate determination of glycols in the samples of runoff water collected from the airport infrastructures. Next, the presented method has been successfully applied to the analysis of samples collected from different international airports.

Keywords: solid-phase microextraction (SPME), gas chromatography-mass spectrometry (GC-MS), de-icing compounds, glycols, stormwater, runoff water

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1. Introduction

Pollution caused by the airport runoff water (stormwater) occurs when the rain transports atmospheric deposits and applied chemicals from the de-icing and cleaning pads, taxiways, runways, apron areas, transfer stations, repair shops and fuel stores to the municipal sewage system and further to the wastewater treatment plants or into surface waters. This can cause serious problems, especially if there is no wastewater treatment plant at the airport, or the existing wastewater treatment plant is malfunctioning [1-7]. Antifreeze fluids containing ethylene glycol (EG), diethylene glycol (DEG) and propylene glycol (PG), which are widely used at the airports for de-icing/anti-icing of aircrafts and runways in cold weather, can pose a specific threat to all compartments of the environment [8-12].

The quantities of aircraft de-icing fluids (ADF), containing mainly EG, PG and DEG, range from 40 L/plane to 15,000 L/plane for large aircrafts during the periods of low temperatures [2]. Due to the large application volume, high loads of these xenobiotics can occur in the airport runoff, especially during the winter season. Consequently, this can contribute to the toxicity of aquatic environment, excessive biological and chemical oxygen demand, and the deterioration of airport infrastructures [13, 14]. The aforementioned analytes are also important by-products of biotransformation pathway of non-ionic surfactants, which are used for cleaning the airport platform and the surface of airplanes [15].

Based on the recently published reports, it has been estimated that the carbonaceous biochemical oxygen demand ($cBOD_5$), and the concentration of EG-ADF and PG-ADF in approximately 50% of solutions used for aircraft de/anti-icing, are ca. 200,000 mg/L and 320,000 mg/L, respectively. Due to the dilution with stormwater and snow melt, the concentration levels of EG-ADF and PG-ADF can reach the values higher than 20,000 mg/L [6, 16]. On the basis of data reported in the literature, it can be concluded that it is necessary to develop analytical protocols for determining glycol pollutants in the samples of airport runoff water, the latter being characterized by the presence of the wide spectrum of potentially interfering substances, complex sample matrices and the occurrence of compounds displaying similar physical and chemical characteristics compared to EG, PG and DEG in stormwater [7, 12, 13].

The extraction of polar small-molecular-weight substances, such as glycols, is a very difficult task and most of the widely used extraction techniques are not fully suitable for this group of compounds. However, matrix interferences are a major problem encountered while determining the content of EG, PG and DEG. Thus the sample matrix must be removed or its

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influence eliminated before proceeding with any analytical determinations. In the case of liquid-liquid extraction or solid-liquid extraction, solvents used at the isolation/enrichment step are often ineffective and may interfere with the analytes [17]. So far, only procedures based on solid-phase extraction (SPE) have been successfully applied to determine glycols in water, as described in our previous study [1]. Nevertheless, the extraction of glycols from the samples containing the airport runoff matrix by means of conventional extraction techniques is difficult [18].

Our increased interest in the development and optimization of modern, reliable and robust extraction and preconcentration techniques has resulted in intensive research in this field. Solid-phase microextraction (SPME) is a modern alternative to traditional extraction methods which have been used for isolating analytes from the runoff water samples. SPME is a very simple, convenient and solvent-free extraction technique which combines extraction, concentration and sample introduction in one step [19, 20]. Therefore, SPME can often be much faster, sensitive, economical and easier to automate as well as it meets the requirements of green chemistry as contrasted with conventional extraction techniques [21-26].

Standard analytical techniques employed to detect and quantify glycols after the isolation or derivatization step include gas chromatography (GC) using mass spectrometry (MS) or flame ionization detector (FID), liquid chromatography–tandem mass spectrometry (LC-MS/MS) as well as colorimetry [14, 15, 27-31]. However, until now, only few data have been published on the determination of EG, PG and DEG in matrices such as plasma, blood, raw sewage, treated sewage, airport sludge and river water [14, 15, 27, 28, 31].

The aim of this research was to develop and validate a new procedure for the determination of antifreeze agents, i.e. ethylene glycol, propylene glycol and diethylene glycol in the airport stormwater samples based on the use of headspace SPME (HS-SPME) coupled with GC-MS. To our knowledge, this is the first time that such an investigation was carried out. Additionally, the developed and validated procedure was successfully applied to the analysis of the samples of airport stormwater collected from different international airports.

2. Material and methods

2.1 Chemicals and Materials

The standards of PG, EG, DEG, EG-d4 in methanol at a concentration of 1,000 µg/mL were purchased from Sigma-Aldrich (Seelze, Germany). Working solutions were prepared by

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diluting the stock solution with water. NaCl was purchased from Merck (Darmstadt, Germany). Deionized water was obtained from Milli-Q water purification system (Millipore Corporation, Bedford, MA, USA).

The SPME holder for manual sampling was purchased from Supelco (Bellefone, PA, USA). Three types of commercially available fibres, i.e. 7-µm polydimethylsiloxane (PDMS), 50/30-µm Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS) and 85-µm polyacrylate (PA) were also obtained from Supelco.

2.2 SPME conditions

The headspace (HS) mode of SPME was used to determine the analytes belonging to glycol group. This type of SPME technique allows for the analysis of samples with complex composition, such as the airport stormwater. In order to minimize the matrix interference, the contact between the sample and the fibre coating must be avoided. In this project, the SPME fibres with different stationary phase coatings were tested and compared. The fibres were conditioned inside the GC injection port by using a nitrogen carrier gas according to the instructions provided by the manufacturer. The HS-SPME extractions were performed in 15-mL glass vials sealed with screw caps containing a septum coated with PTFE/silicone. The headspace-to-sample ratio equaled 3.

In order to determine the optimal extraction conditions, a sample of airport runoff water was spiked with the appropriate amount of PG/EG/DEG mixture (at the concentration level of 1 ppm) and the isotopically labeled standard (internal standard; EG-d4)), was used as a model sample. Before the extraction, the model sample solution was incubated in a vial at the target temperature for 12 min and stirred at 700 rpm. All the model solutions were stirred at the constant maximum speed rate throughout the extraction period to improve the analyte extraction and reduce the extraction time. The analytes were adsorbed from the gas phase onto the stationary phase of the fibre, then the adsorbed organic analytes were thermally desorbed by inserting the fibre into the GC injection system. A possible sample carryover was removed by post-baking of the fibre in the injector for an additional time period in the splitless mode. Additionally, the fibre and blanks were run periodically during the analysis to confirm the cleanliness of the whole GC-MS system. Each extraction was performed in triplicate.

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2.3 GC-MS analysis

Gas chromatography coupled with mass spectrometry was used to determine glycols in the obtained extracts. The conditions of determination for the target compounds were evaluated. The operating conditions together with the retention times and the characteristics of ions employed to quantify EG, PG and DEG are summarized in Table 1.

The schematic presentation of analytical procedure used for the determination of glycols is shown in Fig.1.

Table 1 Operating conditions during GC-MS analysis of glycol extracts.

Element of the measuring system/Parameter	Specification/Analytical conditions		
Gas chromatograph	Agilent 7890A (Agilent Technologies, Palo Alto, CA, USA)		
Detector	Agilent 5975C (Agilent Technologies, Palo Alto, CA, USA)		
Final determination method	GC-EI-MS		
Detector working mode	selected ion monitoring (SIM)		
Ionization source temperature Quadrupole temperature Electron beam energy	230 ^{o}C 150 ^{o}C 70eV		
Chromatographic column	SPB-1000 30m x 0.25mm; 0.25µm film thickness		
Stationary phase of chromatographic column	Acid-modified poly(ethylene glycol)		
Carrier gas pressure	7.65 psi		
Carrier gas flow rate	1.5 mL·min^{-1}		
Injection port temperature	270 ^{o}C		
Interface temperature	300 ^{o}C		
Temperature program	50 ^{o}C (7min) 50-100 ^{o}C (16 ^{o}C/min) 100-200 ^{o}C (10 ^{o}C/min) 200 ^{o}C (5min)		
Analysis time	29 min		
Diagnostic ions (m/z)	Compounds	Retention time [min]	Diagnostic ions (m/z)
	EG	9.6	31; 33
	PG	18.0	45; 75
	DEG	23.2	45; 43

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2.4 *Samples of airport runoff water*

The HS-SPME method was applied to the analysis of 89 samples of airport runoff water collected from the international airports in Great Britain and Poland. The stormwater samples were mostly collected during a continuous precipitation, defined as a steady rain, lasting for at least 5 h. Runoff water was usually collected within 30 min from the beginning of the atmospheric precipitation event (first flush) from the areas of three airports coded as follows: Large Airport PL, Large Airport UK, and Small Airport PL [32]. Samples were collected from the surface depressions near drain inlets and the airport drainage ditches. The sample collection sites were primary located in the areas where the maintenance work has been carried out. The description of sampling sites at the airport platform is presented in Table 2. The airport stormwater samples were collected in 1000 mL bottles made of dark glass by using a syringe (100 mL) with teflon tubing. Prior to use, the syringes and tubing were rinsed with ultrapure water and then with the sampled stormwater. The samples were transported to the laboratory (usually within 1 h after collection, at low temperature). The collected stormwater samples were usually contaminated with solids which had to be pre-filtered (0.45µm, Millex®-HV). No chemicals were added to preserve the samples, therefore, the analyte determinations were initiated immediately after the arrival of samples to the laboratory. The prepared stormwater samples were stored at 4 °C in the dark until further analysis [1, 32-37].

Table 2 The characteristics of sampling sites from which the airport runoff water was collected.

Airports/ Sampling site	Large Airport UK	Large Airport PL	Small Airport PL
1	de-icing area (1)	influent of a river	vicinity of the airport terminal
2	a river in the vicinity of the airport	effluent of a river	de-icing area
3	de-icing area (2)	municipal water catchment area	machinery stock, parking places
4	de-icing area (3)	CARGO water catchment area	runway
5	de-icing area (4)	airport ramp	parking places
6	a road near the airport	car parking lot	the airport periphery
7	-	de-icing area	car parking lot
8	-	airport ramp	-

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3. Results and discussion

3.1 Evaluation of extraction conditions

Several HS-SPME conditions were evaluated to achieve the optimal procedure performance for the analysis of glycols. The following parameters were investigated: the fibre coating selection, extraction time, extraction temperature, desorption time, desorption temperature, the volume of sample and headspace, and the ionic strength. The aforementioned experimental factors have a significant effect on the extraction efficiency of EG, PG and DEG by HS-SPME. The obtained results are presented below, including the discussion part.

3.1.1 Selection of fibre coating

The SPME fibre coating is one of the basic factors which can improve the extraction efficiency. This is due to the strong chemical dependence between the extraction efficiency and the volatility and polarity characteristics of the extracted compounds [38-40]. Three fiber types (PDMS, DVB/CAR/PDMS and PA) were evaluated with respect to the headspace extraction of glycols from the airport runoff water. The performance of each fibre was determined based on the selectivity and the response values, the latter parameter being evaluated from the average peak area of analytes for three repeated analyses [38, 41, 42]. As a result, it was determined that from among the tested fibres only the DVB/CAR/PDMS and PA fibres can be effectively used for the extraction of glycols from the samples of airport stormwater. Fig.2 provides an example of the chromatograms obtained as a result of the HS-SPME of glycols from the airport runoff water using 50/30-µm DVB/CAR/PDMS fibre and 85-µm PA fibre, as presented in Fig.2a and Fig.2b, respectively. On the basis of the obtained data, the 85-µm PA fibre was selected as the optimal fibre coating for the determination of glycols in this study.

3.1.2 Evaluation of extraction time

The HS-SPME is an equilibrium extraction technique, meaning that the time required to reach the equilibrium controls the amount of target compounds extracted with a given fibre, and thus it also controls the sensitivity of the technique [22, 38, 43-45]. Therefore, the extraction time is a very important factor in SPME, and it is necessary to determine the time required for reaching the equilibrium state [20, 46, 47]. However, the practical limitations in terms of analysis must be also taken into consideration [42], and the sorption time profiles were tested by measuring the area counts as a function of exposure time. The fibre was

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exposed to the HS of the model samples for 30 to 60 min. Fig.3a shows the effect of extraction time on the HS-SPME technique. The average recovery values obtained by using a 30-min extraction time were 22% lower than those found after a 40 min extraction. The optimal response values were obtained for the 60-min extraction time which was subsequently chosen as working parameter applied during the sample analysis.

3.1.3 Effects of extraction temperature

As previously mentioned, during the HS-SPME extraction, the distribution and adsorption equilibria of target analytes must be established between the gaseous and aqueous phases, and also between the gaseous and solid phases. The equilibrium depends on various parameters such as, the type of target analytes, the nature of fibre coating, absorption time, and extraction temperature [19]. The influence of extraction temperature was tested at four different temperature levels, i.e. 50, 60, 70 and 80 °C (Fig.3b). The obtained results showed that the amount of analyte adsorbed significantly increases with increasing extraction temperature. The extraction at 80 °C provided the highest efficiency for the tested target analytes. Therefore, the extraction temperature of 80 °C was used to determine the glycols levels.

3.1.4 Study of desorption time and temperature

Desorption time and temperature are crucial factors which ensure a complete recovery of target analyte from the fibre and prevent the risk of carryover. The desorption time profiles were evaluated in the range of 3-7 min (Fig.3c). Furthermore, in order to eliminate sample carryover, the post-baking of the fibre for the additional 5 min was applied. The best response values were observed for the desorption time of 7 min. Under these conditions, no sample carryover was observed. In turn, Fig.3d shows the effect of desorption temperature on the HS-SPME extraction. We observed that the extraction efficiency increased with increasing temperature of the injection port (from 230 to 270 °C). Thus, the desorption temperature of 270 °C was selected for further studies.

3.1.5 Effects of sample and headspace volume

In order to enhance the analytical sensitivity, the volumes of sample and headspace should also be evaluated. The influence of sample and headspace volumes were tested for three different levels of sample volume, i.e. 8 , 10 and 12 mL (Fig.3e). The obtained results

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demonstrated that, in general, the amount of analyte absorbed decreased with increasing sample volume. A sample volume of 8 mL was selected for determining the glycols levels.

3.1.6 Effects of ionic strength

The addition of salt (sodium chloride, NaCl) increases the ionic strength of samples, and thus decreases the solubility of organic analytes and increases the extraction efficiency in case of headspace analysis [23, 38, 42, 48-50]. In order to examine the effect of salt addition on the enrichment of target analytes, different amounts of NaCl, ranging from 1.0 g, 1.5 g to 2.34 g, were added to the model samples. Fig.3f illustrates the effect of salt addition on the HS-SPME extraction. The obtained results show that the amount of analyte extracted by the PA fibre generally increased with increasing salt concentration. It can be noticed that the optimal response values were obtained for the model sample solution containing 1.5 g of added NaCl. Therefore, all HS-SPME extractions were carried out with the addition of 1.5 g of sodium chloride.

3.2 **Quality Assurance/Quality Control (QA/QC)**

In order to evaluate the developed methodology, its selectivity, limit of detection (LOD), limit of quantification (LOQ), linearity of the calibration range, accuracy and repeatability were evaluated. The obtained results are shown in Table 3. The procedure selectivity was evaluated in real samples based on the presence of co-eluting peaks at the analyte retention time: no interfering peaks were observed at the retention times of target analytes. The calibration curves for target analytes were established under optimal HS-SPME and GC-MS conditions. A linear calibration curve was established for each compound by plotting the peak area against the concentration of standards, with the calculated correlation coefficient (R^2). The linear range of the calibration curve was conducted in the range of 0.1-10 mg/L and 10-300 mg/L, respectively. Five independent measurements were carried out for each calibration point [1, 45]. Satisfactory linearity was achieved for the analytes occurring at large concentration ranges. The correlation coefficients of the investigated antifreeze agents varied from 0.985 to 0.996. The LODs were established by calculating the quotient of three times the standard deviation of the intercept and the slope of the calibration curve, while the LOQ was assumed to be equal to three times the LOD. These data were used to establish the method detection limits (MDL) and the method quantification limits (MQL) of the developed methodology by taking into account all necessary analytical steps. The MDL was defined as the lowest concentration of an analyte that can be detected by using the proposed procedure with a specified probability, while the MQL was the lowest

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concentration of a target compound that can be quantified using the analytical methodology with a certain precision, accuracy and uncertainty levels [45]. For the investigated anti-icing compounds, the MQL ranged between 1.30 and 2.80 mg/L. These results are significantly lower than those_reported in the previous study concerning PG and EG determination in the samples of airport runoff water performed by direct injection into the GC-FID system (MQL of 40 mg/L) [51, 52]. The obtained experimental results show that the HS-SPME technique, used for the first time to determine PG, EG and DEG, provides an excellent detection limit without the need for the sample derivatization step. The accuracy of the procedure was established by comparing the measured results to the known spiked concentrations at low, medium and high concentration levels (1, 10, 100 mg/L) of the investigated compounds [24, 53]. The recovery values calculated for the three glycols at all the considered levels were in the range of 67 to 89 %, which means that the procedure can be considered sufficiently accurate [54, 55]. The measurement precision was expressed as the coefficient of variation (CV) according to the following equation: CV=SD/$\overline{X}$*100% ; SD being the standard deviation of the peak area of analyte, while $\overline{X}$ is the average area of the peak. The precision of the method was split into within-run (intra-day, repeatability) and between-run (inter-day, reproducibility) values. The intra-day precision was achieved by preparing samples individually five times and then analyzing them in a single batch during one day. Whereas the inter-day precision was obtained by analyzing the quality control (QC) samples in five replicates on separate days during a period of five days. The numerical values of the intra-day precision were in the range of 10.5-14.3 %. The repeatability values also met the acceptance criterion, i.e. the ≤30 % relative percent difference (RPD) [53]. Generally, the estimated precision met the performance criteria indicating that the reproducible results have been generated. The obtained results are relatively similar to those reported from our previous study, where the SPE/GC-MS procedure was applied to determine glycols in stormawater [1]. The results of recovery experiments by means of the developed SPME/GC-MS procedure were slightly lower in comparison to the recoveries achieved by using the SPE/GC-MS procedure (70-96 %) for the determination of glycols. The SPE/GC-MS procedure is characterized by insignificantly higher precision and the lower value of MQL relative to MQL determined by the SPME/GC-MS method. However, on the basis of literature data and the conclusions resulting from the authors' prior experience, the average concentration levels of glycol in the samples of airport runoff water varied between 50 and 250 mg/L. This confirmed that the values of MQL (1.3-2.8 mg/L) obtained by the SPME/GC-MS methodology are suitable for

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the successful determination of antifreeze agents in stormwater. Moreover, the evaluated SPME/GC-MS procedure offers a wider range of linearity between 0.1 and 300 mg/L, with the higher values of correlation coefficient compared to the R^2 values achieved by using the SPE/GC-MS procedure (0.9700-0.9860) [1].

Table 3 The metrological parameters of the analytical method used for the determination of glycols by using the HS-SPME and GC -MS system.

Analytes	Concentration range of a calibration curve [mg/L]		Calibration curve coefficients (y=ax+b)				R^2		MDL[mg/L]	MQL [mg/L]	Recovery [%]	Inter-day precision [%]
			I		II		I	II				
	I	II	a	b	a	b						
EG	0.1-10	10-300	65482	7123	119104	-1518287	0.9850	0.9930	0.94	2.80	67-79	1.5-17
PG	0.1-10	10-300	61236	- 325.5	93926	- 660731	0.9909	0.9922	0.44	1.30	71-84	0.79-15
DEG	0.1-10	10-300	111927	- 1234.9	291903	-4000000	0.9948	0.9957	0.77	2.30	77-89	1.7-26

3.3 Application to real sample analysis

The content determination of de/anti-icing compounds in the samples of airport runoff water was made by applying the developed and validated analytical methodology based on HS-SPME/GC-MS. The wastewater samples were collected from 2011 to 2013 (40 samples from *Large Airport PL*, 27 samples from *Large Airport UK*, and 22 samples from *Small Airport PL*). Fig.4 illustrates an examplary GC-MS chromatogram of glycols extracted from the runoff water samples collected from the *Large Airport PL* and *Small Airport PL*. According to Fig.4, the extraction methodology for runoff water proved to be effective because there are no interfering peaks that commonly occur on the chromatograms obtained via direct determination of glycols in complex matrices, such as runoff water [1, 2, 45]. The highest peaks in the chromatograms of the tested airport runoff water originate from propylene glycol. As it can be noticed in Fig.4b, all the investigated compounds separated well from the interfering compounds present in the sample collected from the aircraft de-icing area of Small Airport PL.

Fig.5 summarizes the concentration levels of glycols determined in stormwater collected from the monitored airports. The analysis of the obtained data shows that propylene glycol and diethylene glycol were both present at high concentrations in the investigated samples, while the content of ethylene glycol in the samples of airport runoff water was at the trace and even

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ultratrace concentration levels (below the LOQ of the developed procedure). The concentration levels of glycols determined in the samples collected from *Large Airport UK* were in the range of 0.40-3.97 mg/L, while the content of glycols determined in the samples taken from *Large Airport PL* and *Small Airport PL* were in the range of 0.55-1491 mg/L and 0.57-297.9 mg/L, respectively. Generally, the highest concentration levels of target analytes were determined in the samples collected from the aircraft de-icing platforms and airport technical roads. A surprisingly high concentration level of diethylene glycol was observed in the runoff water samples collected from all monitored airports. Diethylene glycol is characterized by the highest toxicity in comparison to other de-icing agents. Because of that, DEG should be excluded from de/anti-icing mixtures. The obtained data show that the level of environmental pollution at the airport infrastructure is not always simply correlated with the airport capacity or its size. In most cases, the big international airports, such as the monitored *Large Airport UK*, have greater budgets to create the infrastructure management system, e.g. on-site wastewater pre-treatment and treatment plants or the system for waste re-circulation, together with the use of ecological de-icing agents and detergents. That can results in a significant reduction in the emission of pollutants generated by the airports [32].

4. Conclusions

As a result of the performed research, a new methodology has been developed, which is based on the green extraction technique- SPME and GC-MS for the determination of antifreeze substances in the samples of airport runoff water. The obtained experimental data show that the HS-SPME technique is a powerful method for extracting de/anti-icing compounds from the airport stormwater samples without the need for the analyte derivatization. The HS-SPME method combines sampling, extraction and cleanup of glycols from the airport sludge in a single step. The HS-SPME–GC/MS procedure presented here allowed the rapid, sensitive, precise, accurate and inexpensive identification and quantification of PG, EG and DEG in the samples of airport runoff water. Considering the previously published reports, it can be stated that the proposed methodology is suitable for extensive controlling of aquatic pollution with glycols.

Acknowledgments

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Figure captions

Fig. 1 Schematic presentation of analytical procedure for the determination of glycols in the samples of airport runoff water by using HS-SPME and GC-MS system.

Fig. 2 Total ion current (TIC) chromatograms obtained after HS-SPME in order to determine glycols in the samples of airport runoff water by using different fiber coatings, namely, (a) 50/30-µm DVB/CAR/PDMS, and (b) 85-µm PA.

Fig. 3 Evaluation of the HS-SPME conditions for determining glycols in the samples of runoff water.

Fig. 4 Chromatograms obtained for the stormwater samples collected on 31 Jan, 2013 (a) from the aircraft de-icing area of Large Airport PL, and on 23 Feb, 2013 (b) from the aircraft de-icing area of Small Airport PL by using the HS-SPME/GC-MS procedure.

Fig. 5 Concentration levels of glycols determined in the samples of stormwater collected from different areas of three airports (Large and Small Airport PL, and Large Airport UK).
*Propylene glycol concentration levels in samples collected from Large Airport PL on 14 Jan, 2013 exceeded the range of calibration curves and were thus estimated by extrapolation.

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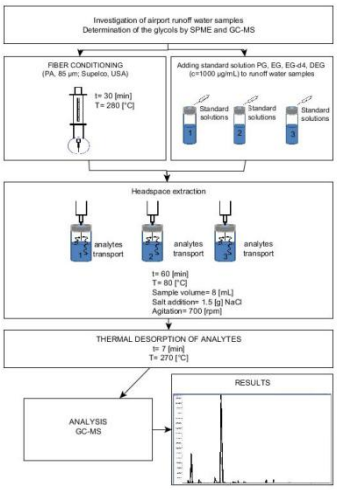

Figure 1

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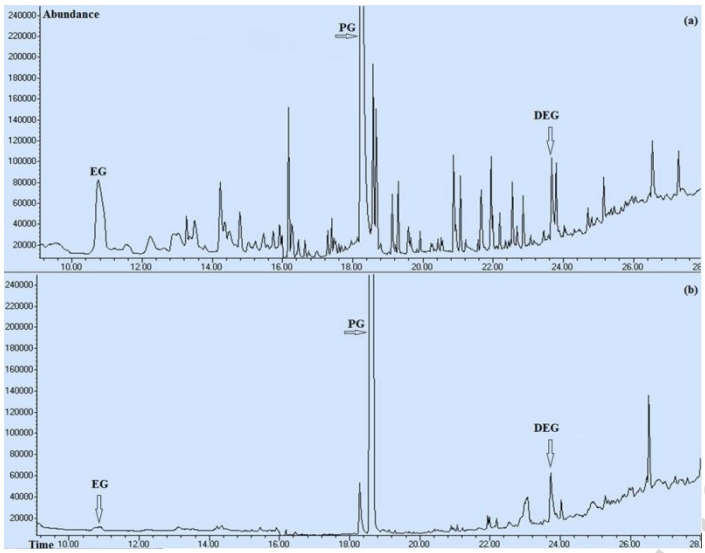

Figure 2

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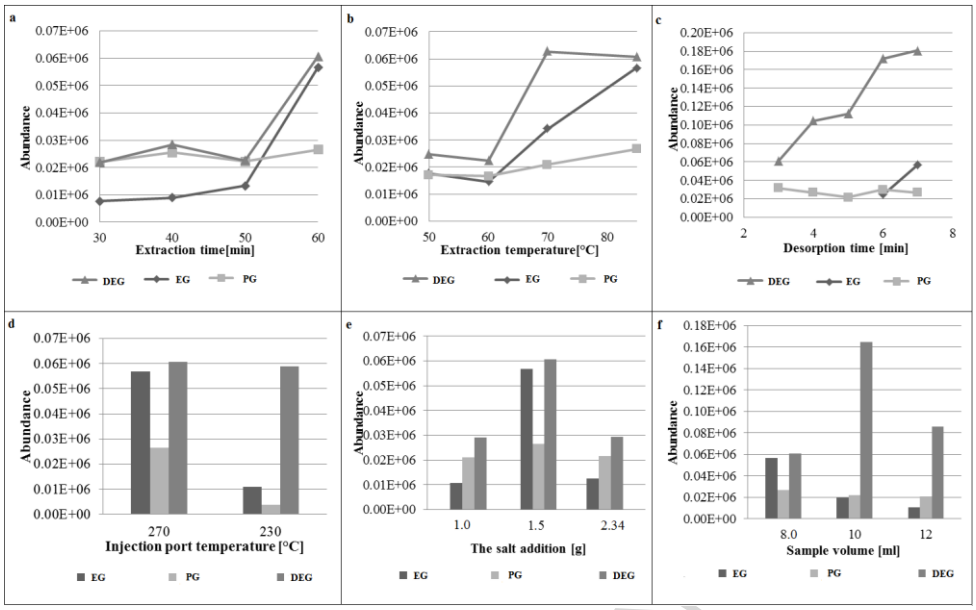

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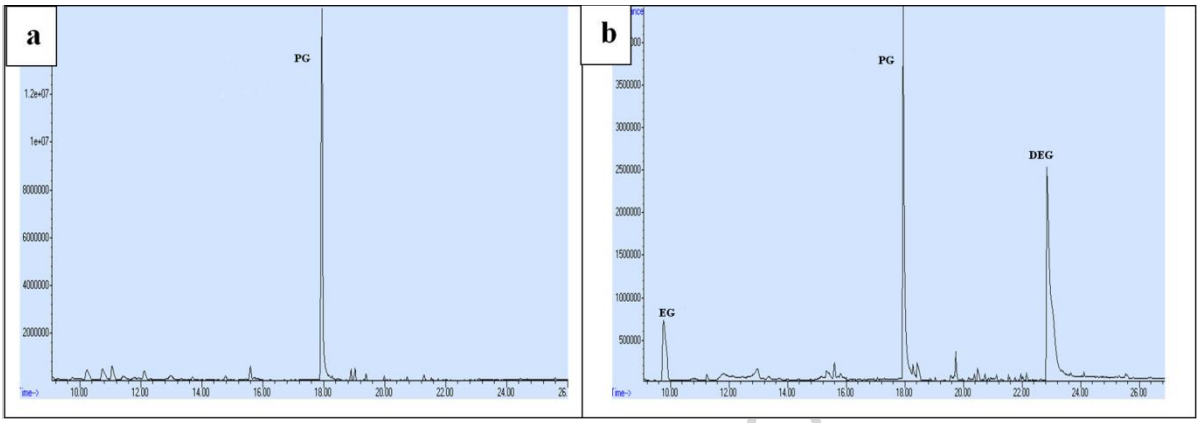

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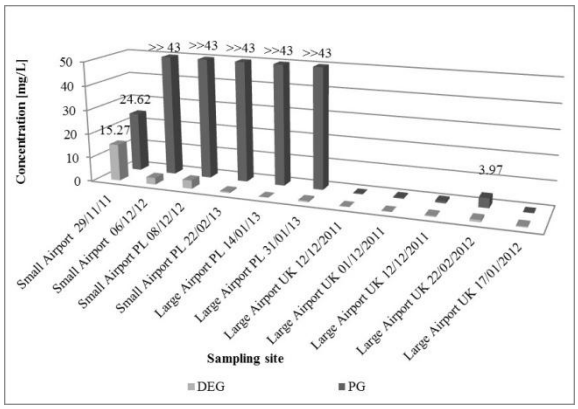

Figure 5

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Highlights

1. Analysis of new type of environmental samples - airport runoff water
2. Analytical method based on HS-SPME–GC/MS was developed for glycols determination
3. The method allowed the rapid, precise, accurate determination of antifreezers
4. The procedure was successfully applied to 89 airport runoff water samples
5. New procedure as tool for an extensive control of pollution of waters by glycols

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