Cumhuriyet Science Journal
CSJ

e-ISSN: 2587-246X
ISSN: 2587-2680

Cumhuriyet Sci. J., Vol.39-4(2018) 970-982

Gas Chromatography Method Validation Study for Sensitive and Accurate Determination of Volatile Aromatic Hydrocarbons (VAHs) in Water

Barış GÜZEL*, Oltan CANLI, Elmas ÖKTEM OLGUN

TÜBİTAK Marmara Research Center, Environment and Cleaner Production Institute, Kocaeli, TURKEY,

Received: 02.07.2018; Accepted: 01.11.2018 *http://dx.doi.org/10.17776/csj.439764*

Abstract. A wide range of chemicals comes to exist at the end of the industrial activities. They could have highly toxic and carcinogenic effects on the human health and water environment. Therefore, these substances, which are listed as prohibited chemicals on national and international lists, must be monitored permanently with regards to environmental and human health both in the water resources and potential receiving waterbodies. The objective of this study was to present the method for the sensitive and accurate determination of some volatile aromatic hydrocarbons (VAHs), including quite dangerous substances such as benzene, toluene, xylenes, styrene and chlorobenzenes by using gas chromatography - mass spectrometry (GC-MS) with purge & trap (PT) process in different water samples. The proposed method was verified with the selectivity, linearity, limits of detection and quantification (LOD and LOQ), precision studies of the method and instrument. All analytes examined in the study were trustworthily measured within the maximum performance limits for PT-GC-MS. The selectivity work was carried out by duplicate analysis of six blank water samples. There is no finding or observation within the interval of the retention time of the analytes in the water samples. The linearity of calibration curves was drawn by analysis of prepared standard solutions at nine concentration levels. The analytical response linearity in the working range can be assessed as an excellent since the correlation coefficients higher than 0.9996 for all analytes. The method accuracy was carried out by doing recovery experiment. Recoveries of analytes have been changed from 88.4 % to 94.6 % and the relative standard deviation (RSD) results were found between 3.52 % and 6.35 %. The applicability of developed method was confirmed by the determination of related analytes in the water samples.

***Keywords*:** Gas chromatography, purge & trap, quantitative analysis, volatile aromatic hydrocarbon, water.

Suda Uçucu Aromatik Hidrokarbonların (UAH'lar) Hassas ve Doğru Analizi için Gaz Kromatografisi Yöntemi Doğrulama Çalışması

Özet. Endüstriyel faaliyetlerin sonucunda çok çeşitli kimyasallar ortaya çıkmaktadır. Bunlar, insan sağlığı ve su ortamı üzerinde oldukça toksik ve kanserojenik etkilere sahip olabilirler. Bu nedenle, ulusal ve uluslararası listelerde yasaklanmış kimyasallar olarak yer alan bu maddeler, hem su kaynakları hem de potansiyel alıcı su ortamlarında çevre ve insan sağlığı açısından sürekli olarak izlenmelidir. Bu çalışmanın amacı, farklı su örneklerinde tasfiye & tutma (PT) işlemi ile gaz kromatografisi - kütle spektrometresi (GC-MS) kullanılarak benzen, toluen, ksilenler, stiren ve klorobenzenler gibi oldukça tehlikeli maddeler içeren bazı uçucu aromatik hidrokarbonların (UAH'lar) hassas ve doğru tespitine yönelik yöntemi sunmaktır. Önerilen metot, seçicilik, doğrusallık, tespit ve tayin limitleri (LOD ve LOQ), metot ve cihazın kesinlik çalışmaları ile doğrulanmıştır. Çalışmada incelenen tüm analitler, PT-GC-MS için maksimum performans sınırları içinde güvenilir şekilde ölçülmüştür. Seçicilik çalışması, altı boş su örneğinin çift analizi ile gerçekleştirilmiştir. Su örneklerindeki analitlerin alıkonma süreleri arasında herhangi bir bulgu veya gözleme rastlanmamıştır. Kalibrasyon eğrilerinin doğrusallığı, dokuz konsantrasyon seviyesinde hazırlanan standart çözeltilerin analizi ile çizilmiştir. Çalışma aralığındaki analitik tepki doğrusallığı, tüm analitlerin korelasyon katsayıları 0,9996 'dan büyük olduğu için mükemmel olarak değerlendirilebilir. Metot doğruluğu, geri kazanım deneyi yapılarak gerçekleştirilmiştir.

---

* Corresponding author. *Email address: baris.guzel@tubitak.gov.tr, guzelbaris08@gmail.com*

Analitlerin geri kazanımları % 88,4 ile % 94,6 arasında değişmektedir ve bağıl standart sapma (RSD) sonuçları % 3,52 ile % 6,35 arasında bulunmuştur. Geliştirilen metodun uygulanabilirliği, su örneklerinde ilgili analitlerin tespiti ile doğrulanmıştır.

Anahtar Kelimeler: Gaz kromatografi, tasfiye & tutma, kantitatif analiz, uçucu aromatik hidrokarbon, su.

1. INTRODUCTION

Rapidly growing human population leads to environmental problems along with the urbanization and industrialization activities. Although industrialization activities have a positive effect on facilitating human life economically, they reveal serious problems about human health and environmental pollution. Water, which is one of the main sources of living organisms, is significantly affected by these activities that cause these environmental pollutants [1]. If persistent and toxic chemicals such as heavy metals, pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), dioxins/furans (PCDD/Fs), volatile organic compounds (VOCs) and sulfur dioxide (SO_2) emerged at the end of the industrial processes are in the water environment, they pose a risk to the environment and causes important health problems such as cancer in terms of human health. Furthermore, these substances, exposure even in small quantities over long time, cause bioaccumulation in the tissues of the human body [2].

VAHs, which are subgroup of VOCs, have also been a significant class of organic pollutants in the worldwide recently because of several negative effects. Thus, they should be analyzed the type and quantity of them especially in environmental waters to reduce their toxic impacts and to monitor for human life [3-7]. VAHs are organic chemicals and composed of carbon chains and their derivatives. They have high vapor pressure at room temperature [8]. In accordance with D3960 test method of American Society for Testing and Materials (ASTM), they have a vapor pressure greater than 13.3 Pa (0.1 mm Hg) at 25 °C [9].

Detection of trace amounts of volatile compounds in aqueous and liquid matrices is still an ongoing problem for gas chromatographic systems. For solving this problem, important works have been done in this area and many methods have been reached to the present day. A substantial majority of these methods contains one or more intermediate steps in which the desired analytes are isolated from water environment and intensified prior to GC analysis [10-12]. Some special equipments such as passive badges, canisters and sorbent traps are used for the determination of volatile compounds and separation process have been carried out with gas chromatography with flame ionization detection (GC–FID) or with GC–MS in general [13]. In volatile compound analysis, GC-MS system is one of the most valuable techniques due to its high sensitivity and selectivity. However, a sufficient extraction process is usually necessary prior to GC-MS analysis to specify the small quantities of volatile compounds in water samples. PT and solid-phase microextraction (SPME) methods are the most chosen analysis and also sample pre-concentration methods on account of gorgeous recoveries for a great quantity of volatile compounds. At the present time, PT method is the most valuable and applicable method for preparing water samples for volatile compound analysis and in addition to this, critical quantification for several volatile compounds in water has been performed by the automatization of PT process fully with GC–MS systems [14-16]. The advantage of this system is that it picks up only the volatile analytes of interest by eliminating non-volatile compounds and provides the measurement of low detection limits [10]. The analysis of volatile compounds in the PT-GC-MS was performed at first purging of volatile compounds from water samples by using a stream of gases and then, they were adsorbed a trap which is made of porous solid sorbent and were desorbed into GC system for separation and quantitation processes. It has been indigenized by several organizations such as EPA in their analysis methods [17, 18]. The measurement condition of PT process such as sample temperature, purge time, flow rate of purge gas, type of adsorbent in the trap, temperature of the trapping tube at purging and heating times for the analysis of volatile compounds must be always monitored most certainly in detail. Furthermore, water samples cannot include foaming substances and should be without solid suspensions to be measurable by the conventional PT method [19].

The objective of this work was to develop the simultaneous determination of sixteen water soluble VAHs, including highly toxic substances such as benzene, toluene, xylenes, styrene with PT method in the drinking water, seawater and wastewater samples. This paper describes the following validation parameters for simultaneous analysis of VAHs: selectivity, calibration curve linearity, limits of detection and quantification (LOD and LOQ), precision studies of the method and instrument according to [10,11,14,15,20,21]. The recovery studies of each analytes from drinking water, seawater and wastewater samples was also examined. The applicability of the developed PT method was confirmed by the determination of VAHs in the different matrix samples of water.

2. MATERIALS AND METHODS

The conducted studies with in the context of this research were actualized in the accredited laboratories of The Scientific and Technological Research Council of TURKEY Marmara Research Center (TUBITAK MAM) Environment and Cleaner Production Institute, which possessnational accreditation certificates taken from Turkish Accreditation Agency (TURKAK) pursuant to TS EN ISO/IEC 17025:2012 standard since July 16, 2010 and international accreditation certificates acquired from German Accreditation Council DAR/DAP (Deutscher Akkreditierung Rat) since December 17, 2002. These laboratories were also obtained on February 21, 2011 to “Measurement and Analysis of Environmental Qualification Certificate” from the Republic of Turkey Ministry of Environment and Urbanization.

2.1. Reagents and Chemicals

Standard sample solution including 60 different VOCs (200 mg/L each in methanol) was supplied by High-Purity Standards Co., Inc. (North Charleston, USA). Ampoule of 1,2,3-trichlorobenzene in methanol with purities higher than 99% was purchased from Dr. Ehrenstrofer (Ausburg, Germany). The investigated VAHs in this study and some properties such as boiling points, retention times and selected masses are listed in Table 1. 4-bromofluorobenzene (25 mg/mL in methanol) used as the internal standard (IS) for quality assurance in the analysis of VOCs were obtained from Absolute Standards Co., Inc. (Hamden, USA). Milli-Q Plus system (EMD Millipore, Billerica, MA) was used for the purification of water used to prepare the necessary solutions. Methanol as a solvent used in the preparation of stock standard solutions was highest purity grade and supplied from Merck (Darmstadt, Germany).

A stock standard solutions were prepared in methanol mixing with 200 mg/L VOC standard sample solution and 100 mg/L 1,2,3-trichlorobenzene at concentration of 1 mg/L and 10 mg/L and they were stored at 1.5 ml vials maintained in freezer (-20 °C). These solutions can be used for a period of one month. At the end of the one-month period, they should be prepared again. Standard VAH solutions used in measurement were prepared daily in 50 ml volumetric flask by dilution of 1 mg/L and 10 mg/L of stock standard VAH solutions in distilled water.

Table 1. Boiling points, retention times and selected masses of VAHs [22-24].

Compound	Boiling point (°C)	Retention time (min)	Target ion (m/z)	Quantified ion (m/z)
Benzene	80	7.62	77	78
Toluene	111	10.90	91	92
Ethylbenzene	136	14.17	91	106
P&M-Xylene	138-139	14.47	91	106
Styrene	145	15.21	91	103
O-Xylene	144	15.25	91	106
4-bromofluorobenzene (IS)	152	16.20	95	174
Isopropylbenzene	151	16.25	105	120
N-Propylbenzene	159	17.18	91	120
1,3,5-Trimethylbenzene	165	17.68	105	120
1,2,4-Trimethylbenzene	168	18.45	105	120
1,3-Dichlorobenzene	173	18.87	146	148
1,4-Dichlorobenzene	174	19.14	146	148
1,2-Dichlorobenzene	180	19.70	146	148
1,3,5-Trichlorobenzene	208	22.40	180	182
1,2,4-Trichlorobenzene	214	23.59	180	182
1,2,3-Trichlorobenzene	218	24.44	180	182

2.2. Water Samples

Three different types of water samples were used in this study. These are drinking water, seawater and wastewater. Drinking water samples in 1000 mL glass bottles were purchased from supermarket stores in Gebze, Kocaeli. Seawater samples were collected in 250 mL glass bottles at 500 m away from the port of Fener (Rumelifeneri, Sarıyer) in Black sea region. Wastewater samples were obtained in 100 mL glass bottles from Istanbul Water and Sewerage Administration (ISKI) wastewater treatment plant in Kadıköy, Istanbul. Sample bottles were filled wholly without bubbles and capped tightly. All the samples were stored at less than 5 °C until they were analyzed. Similar sample storage condition for analysis of VAHs was used by Ueta and co-workers [15].

2.3. Analytical Instrumentation

2.3.1. GC-MS Analytical Condition

Agilent Technologies 6890N network GC system (Avondale, USA) coupled with 5975C inert mass spectrometer with triple detector (MSD) was carried out for the determination and quantification of VAHs and a DB-5MS fused silica capillary column having 60 m × 0.25 μm with a 0.25 μm film thickness (Agilent Technologies J&W Scientific, Folsom, CA, USA) was used as analytical column in GC separation. A split mode was employed in all injections with a ratio of 20:1 by using a 4.0 mm split liner at 200 °C. High purity helium gas (99.9995 %) was used as the carrier gas with the pressure of 110 kPa in the port of injection. Gas flow rate was 1.0 mL/min. The adjustment of initial temperature and ionization voltage of GC system was performed to 280 °C and 70 eV by selecting electron impact ionization. At the beginning, the column temperature was set to 40 °C for 2 min and operated to increase to 200 °C at a rate of 7 °C /min. When the system was reach final temperature, it was held for 5 min. MS was programmed to a total-ion-monitoring mode (m/z: 25-550). The quantification of each VAH was actualized with relevant target and quantified ions, as summarized in Table 1.

2.3.2. PT Analytical Condition

PT process was performed using OI Analytical Eclipse model 4660 sample concentrator (College Station, TX, USA) equipped with a OI Analytical 4552 water/soil autosampler. A 50 mL glass vial was filled with prepared aqueous standard VAHs' sample. Afterwards, 25 ml of this sample were transferred to the purge unit by injector adding IS. Then, sample was purged by supplying pure helium gas as the purge gas. Volatile compounds were collected by trap unit (VOCARB 4000 Trap). Consequently, collected volatile compounds were sent to the GC column by desorbing from the trap. The conditions of PT instrument throughout the experiments are summarized as follows: purgeready temperature: 35 °C, purge time: 11 min, dry purge time: 5 min, desorb preheat: 180 °C, desorb time: 1 min, desorb temperature: 180 °C, bake time: 7 min, bake temperature: 260 °C.

2.4. Method Validation

The validation process of proposed method was actualized in accordance with the Commission Decision EURACHEM Guideline [21] and Guidelines for Standard Method Performance Requirements [25]. The following parameters were evaluated in this method: selectivity, calibration curve linearity, recovery (accuracy), reproducibility, limits of detection and quantification.

3. RESULTS AND DISCUSSIONS

3.1. Validation Study

3.1.1. Selectivity

The selectivity study was performed by the duplicate analysis of six blank water samples. At the end of the analysis, there is no observation about the peaks of interfering compounds throughout range from retention time of working analytes in these water samples.

3.1.2. Linearity

Linearity of curve can be defined as the coefficient of linear correlation (r) and from the slope of the calibration curve The linearity of calibration curves in this study was established by analyses of calibration standard solutions of VAHs at nine 0.15, 0.25, 0.5, 1, 2, 5, 10, 20 and 40 µg/L concentration levels prepared from 1 mg/L and 10 mg/L stock standard VAH solutions. The results of linearity study for the investigated VAHs are given in Table 2 and besides, the plots of calibration curves of some VAHs are shown in Figure 1. The analytical response linearity in the working concentration range can be assessed as an excellent on the occasion of correlation coefficients higher than 0.9996 for all analytes. Similar findings for linearity of some VAHs were obtained in the studies of [16, 24].

Table 2. Linearity study of investigated VAHs.

Compound	Coefficient correlation (r^2)	Calibration curve equation
Benzene	0.9997	y = 75303x + 9609,7
Toluene	0.9996	y = 97609x + 97944
Ethylbenzene	0.9999	y = 121781x + 6841,1
P&M-Xylene	0.9997	y = 44856x - 9081,3
Styrene	0.9999	y = 57766x - 10087
O-Xylene	0.9998	y = 93040x - 2895,5
Isopropylbenzene	0.9996	y = 133550x + 18469
N-Propylbenzene	0.9998	y = 236680x + 35492
1,3,5-Trimethylbenzene	0.9999	y = 112267x + 11792
1,2,4-Trimethylbenzene	0.9998	y = 107730x + 14524
1,3-Dichlorobenzene	0.9996	y = 44536x - 5264,9
1,4-Dichlorobenzene	0.9996	y = 39184x - 2500,3
1,2-Dichlorobenzene	0.9999	y = 31839x - 3378,3
1,3,5-Trichlorobenzene	0.9999	y = 31299x + 168,14
1,2,4-Trichlorobenzene	0.9999	y = 17134x - 2202,7
1,2,3-Trichlorobenzene	0.9997	y = 9467,3x - 894,31

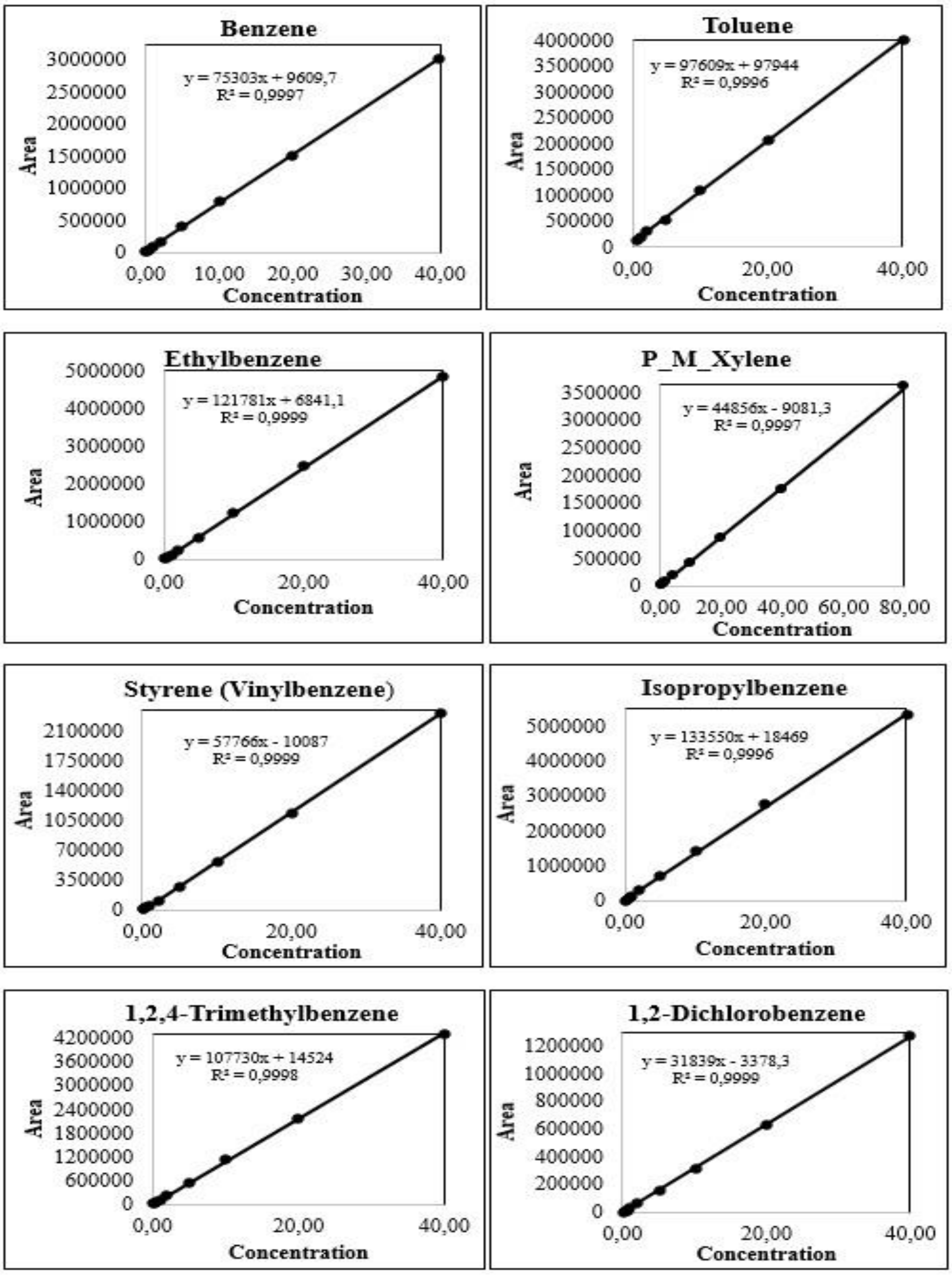

Figure 1. The plots of calibration curves of some VAHs.

3.1.3. LOD and LOQ

The sensitivity of this method was evaluated with the determination of LOD and LOQ values. LOD and LOQ results were computed from the mean noise value in chromatogram by analyzing eight 5 µg/L standard VAH solutions, and they were determined by multiplying the values of mean noise by 3 and 10, respectively. The results of LOD and LOQ are given in Table 3. Thus, LOD values for VAHs was achieved from 0.01 to 0.02 µg/L, and the range of LOQ for VAHs was obtained from 0.02 to 0.08 µg/L. These results are found comparable with the results of similar studies of [4, 15, 26]. Besides, Alonso et al. [24] found LOD and LOQ values higher than for relevant analytes our LOD and LOQ values.

Table 3. LODs and LOQs of investigated VAHs.

Compound	LOD (µg/L)	LOQ (µg/L)	RSD (%)
Benzene	0.01	0.02	0.22
Toluene	0.01	0.02	0.20
Ethylbenzene	0.01	0.02	0.17
P&M-Xylene	0.01	0.02	0.21
Styrene	0.01	0.04	0.42
O-Xylene	0.01	0.02	0.23
Isopropylbenzene	0.01	0.02	0.15
N-Propylbenzene	0.02	0.05	0.54
1,3,5-Trimethylbenzene	0.01	0.02	0.19
1,2,4-Trimethylbenzene	0.01	0.02	0.20
1,3-Dichlorobenzene	0.01	0.06	0.58
1,4-Dichlorobenzene	0.01	0.06	0.64
1,2-Dichlorobenzene	0.01	0.08	0.77
1,3,5-Trichlorobenzene	0.01	0.03	0.29
1,2,4-Trichlorobenzene	0.01	0.03	0.28
1,2,3-Trichlorobenzene	0.02	0.07	0.73

RSD: Relative standard deviation

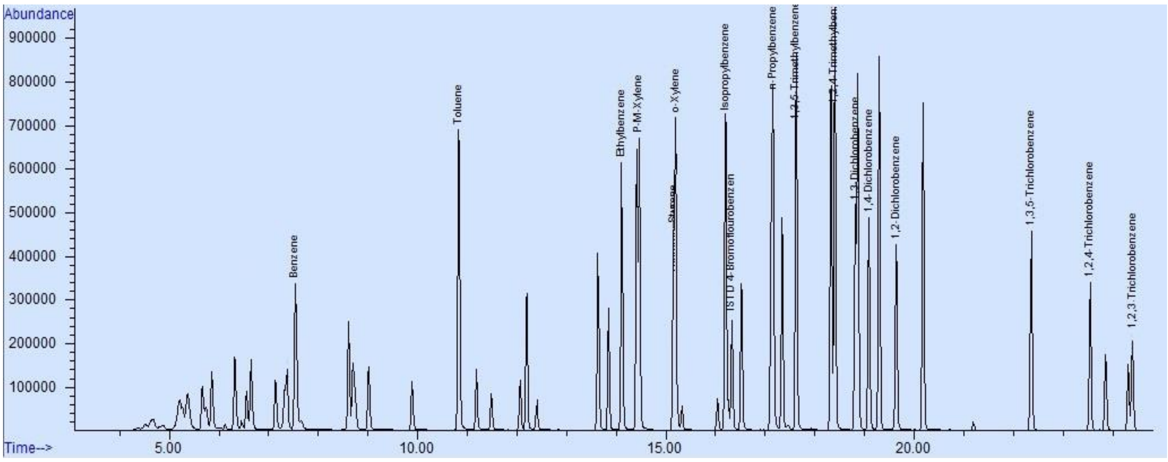

Figure 2. shows the chromatogram of 5 µg/L standard VAH solution, which is used for the determination LOD and LOQ levels of investigated VOCs.

3.1.4. The Accuracy of Method

The accuracy of this method was determined by performing the recovery experiment. This experiment was carried out for VAHs in water with eight sequential measurements at two different concentrations (2 µg/L and 5 µg/L). Detailed results about the average recovery and percentage of RSD for the accuracy of the method are summarized in Table 4. The percentage of recovery is calculated the percentage ratio of the measurement value to the theoretical value. In accordance with the Table 4, it is clear that mean recoveries of VAHs obtained at the end of the experiment are quite gratifying ranging from 88.4 % to 94.6 % and the RSD results were found between 3.52 % and 6.35 %. These results demonstrate that this method is rather good and sufficient capability for the accurate analysis of VAHs in water and the accuracy results of the method in Table 4 were verified the values given in [25]. Furthermore, the accuracy of parameters except 1,3,5-Trichlorobenzene were checked with a certified reference material (CRM).

Table 4. Recovery test results of investigated VAHs.

Compound	Mean recovery (%)	RSD (%)
Benzene	89.4	4.44
Toluene	91.8	4.96
Ethylbenzene	91.4	4.61
P&M-Xylene*	90.6	4.55
Styrene	88.4	4.42
O-Xylene	94.1	3.56
Isopropylbenzene	91.5	6.35
N-Propylbenzene	92.0	4.83
1,3,5-Trimethylbenzene	93.6	3.84
1,2,4-Trimethylbenzene	93.9	5.20
1,3-Dichlorobenzene	93.1	5.43
1,4-Dichlorobenzene	93.2	5.70
1,2-Dichlorobenzene	94.9	3.52
1,3,5-Trichlorobenzene	92.8	4.97
1,2,4-Trichlorobenzene	94.6	3.54
1,2,3-Trichlorobenzene	94.6	4.56

* Measurement of p&m-xylene was performed for 4 µg/L and 10 µg/L standard VAH solutions.

3.1.5. The Precision of Method

The method precision was made a decision and was evaluated by performing intra-day and inter-day studies. These studies were expressed as the RSD according to the conditions for repeatability and reproducibility, respectively. The intra-day precision (repeatability) were carried out on the same day using the same instrument by sequential measurements with two standard VAH solutions with concentration values of 2 µg/L and 5 µg/L prepared by using 10 mg/L of stock standard VAH solutions in distilled water to determine standard deviation (SD) and the percentage of RSD. For each concentration level, six measurements were made. As a result of the measurement, mean measured concentration values, SD, the repeatability expressed RSD in Table 5 were obtained. For these concentration levels interpreted in the study of intra-day precision, the RSD values suggested should be below 20 % [25]. It is obvious that the values of RSD in the intra-day study were found ranging from 1.76 % to 6.93 %. Therefore, this method indicated convenient intra-day precision.

The inter-day precision (reproducibility) was evaluated by data generated on different days, listed in Table 6, was examined at 5 µg/L concentration levels. The number of measurements for this concentration level both two days was six. As observed from Table 6 that mean difference from two days ranged between 2.19 % to 5.92 % under the conditions for inter-day reproducibility. Therefore, the precision results of this method (Table 5 and Table 6) conform to the values given in [25]. Besides, the authors [24, 27] found precision and accuracy results expressed RSD higher than ours for some analytes such as benzene, toluene, xylenes, n-propylbenzene and trichlorobenzenes.

Table 5. Repeatability results of investigated VAHs.

Compound	No of injections (5 µg/L)									No of injections (2 µg/L)								
	1	2	3	4	5	6	Average	SD	RSD (%)	1	2	3	4	5	6	Average	SD	RSD (%)
Benzene	4.861	4.685	4.765	4.775	4.607	4.776	4.745	0.088	1.85	1.976	1.934	1.959	1.790	1.863	1.815	1.890	0.078	4.13
Toluene	4.800	4.600	4.629	4.686	4.539	4.643	4.650	0.088	1.90	2.086	2.044	2.058	1.869	1.963	1.901	1.987	0.089	4.50
Ethylbenzene	4.877	4.688	4.725	4.796	4.649	4.696	4.739	0.084	1.76	2.094	2.039	2.042	1.928	1.855	1.844	1.967	0.106	5.38
P&M-Xylene*	9.760	9.368	9.409	9.555	9.283	9.432	9.468	0.169	1.78	4.229	4.150	4.170	3.758	3.951	3.810	4.011	0.200	4.98
Styrene	4.505	4.421	4.256	4.354	4.297	4.295	4.355	0.093	2.14	1.646	1.655	1.669	1.608	1.592	1.606	1.629	0.032	1.94
O-Xylene	4.926	4.785	4.437	4.828	4.769	4.783	4.755	0.166	3.49	2.086	2.063	2.076	1.919	2.002	1.939	2.014	0.073	3.60
Isopropylbenzene	4.911	4.694	4.691	4.753	4.577	4.697	4.720	0.110	2.32	2.106	2.043	2.071	1.785	1.913	1.828	1.958	0.135	6.88
N-Propylbenzene	4.974	4.730	4.720	4.791	4.640	4.710	4.761	0.115	2.41	2.161	2.101	2.125	1.826	1.957	1.865	2.006	0.143	7.12
1.3.5-Trimethylbenzene	4.923	4.736	4.682	4.758	4.599	4.709	4.735	0.108	2.28	2.109	2.062	2.082	1.848	1.966	1.878	1.991	0.110	5.55
1.2.4-Trimethylbenzene	5.038	4.879	4.414	4.866	4.728	4.808	4.789	0.210	4.39	2.135	2.102	2.117	1.935	2.017	1.949	2.042	0.088	4.29
1.3-Dichlorobenzene	5.133	5.069	4.893	4.997	4.889	4.910	4.982	0.102	2.05	2.064	2.056	2.073	1.884	2.022	1.990	2.015	0.071	3.52
1.4-Dichlorobenzene	5.156	5.149	4.748	5.019	4.916	4.913	4.984	0.157	3.15	2.065	2.043	2.064	1.915	2.028	1.992	2.018	0.057	2.83
1.2-Dichlorobenzene	5.151	5.203	4.879	4.988	4.888	4.896	5.001	0.143	2.86	2.006	2.010	2.022	1.926	1.993	1.984	1.990	0.034	1.72
1.3.5-Trichlorobenzene	5.010	4.958	4.613	4.754	4.648	4.639	4.770	0.173	3.63	2.116	2.091	2.101	1.965	2.022	1.979	2.046	0.066	3.21
1.2.4-Trichlorobenzene	5.011	5.218	4.575	4.735	4.641	4.616	4.799	0.258	5.38	2.027	2.046	2.055	1.940	2.010	2.036	2.019	0.042	2.06
1.2.3-Trichlorobenzene	5.206	5.927	4.901	5.141	5.100	5.039	5.219	0.362	6.93	2.046	2.096	2.098	2.058	2.072	2.058	2.072	0.022	1.04

* Measurement of p&m-xylene was performed for 4 µg/L and 10 µg/L VAH solutions.

Table 6. Reproducibility studies of investigated VAHs.

Compound Name	Conc. (µg/mL)	VOC spiking solution injected on day 1							VOC spiking solution injected on day 2							Difference (%)
		Area 1	Area 2	Area 3	Area 4	Area 5	Area 6	Average	Area 1	Area 2	Area 3	Area 4	Area 5	Area 6	Average	
Benzene	5.23	1135203	1090507	1109043	1158634	1149557	1063488	1117739	1075232	1102951	1069468	1048211	1092806	1013768	1067073	4.53
Toluene	5.15	1438130	1398349	1439090	1393057	1404557	1353838	1404504	1362365	1409208	1358881	1328991	1371219	1273206	1350645	3.83
Ethylbenzene	5.25	1721434	1656806	1635225	1604132	1628946	1597237	1640630	1617953	1570807	1603035	1544748	1603684	1584619	1587474	3.24
P&M-Xylene*	10.33	4443770	4297762	4516436	4278068	4461974	4148604	4357769	4194533	4304765	4143131	4001593	4132440	3847542	4104001	5.82
Styrene	5.18	941044	929943	997214	930984	944881	921995	944344	916535	930858	906902	892698	898250	850025	899211	4.78
O-Xylene	5.23	1488062	1455703	1481477	1436435	1513979	1418919	1465763	1431966	1449358	1401047	1381493	1415048	1331491	1401734	4.37
Isopropylbenzene	5.15	1893433	1798703	1798565	1754093	1857206	1713342	1802557	1756160	1806718	1731111	1650783	1729767	1602301	1712807	4.98
N-Propylbenzene	5.08	544153	516297	471131	481950	528537	491370	505573	504283	520350	497448	469911	485184	447552	487455	3.58
1,3,5-Trimethylbenzene	4.99	1751676	1683854	1643294	1677515	1730916	1621762	1684836	1646496	1674143	1613329	1568854	1606789	1499953	1601594	4.94
1,2,4-Trimethylbenzene	5.00	1880239	1840362	1885405	1825071	1889746	1788629	1851575	1802839	1824001	1764203	1728105	1743441	1651470	1752343	5.36
1,3-Dichlorobenzene	4.83	902879	966087	959991	923940	927006	937790	936282	934153	946105	924751	916364	907202	866313	915815	2.19
1,4-Dichlorobenzene	4.79	955702	945120	981805	995585	953444	916903	958093	918689	926498	901797	894710	883820	898575	904015	5.64
1,2-Dichlorobenzene	4.70	837522	830441	858784	865576	842003	814282	841435	809614	815681	794647	796479	787716	760848	794164	5.62
1,3,5-Trichlorobenzene	4.76	805387	823100	802580	851673	817958	787432	814688	790697	805465	778452	770797	733532	728159	767850	5.75
1,2,4-Trichlorobenzene	4.86	599353	601090	553971	511130	597683	579591	573803	575713	582722	567362	559913	537994	515250	556492	3.02
1,2,3-Trichlorobenzene	4.82	395551	423822	429293	428630	423696	411386	418730	404744	411738	402131	385079	388490	371583	393961	5.92

* Measurement of p&m-xylene was performed for 10 µg/L standard VAH solution.

3.1.6. Matrix effects

Assessment of matrix effect is significant point for the validation study of analytical method of VAHs by using the GC-MS P&T technique. Because, matrix interferences can affect the ionization efficiency of the analytes in MS source. Matrix effect is evaluated with the rate of signal suppression or enhancement which is obtained from the behaviour of the different matrices of the standard solution. The resulting values less than 100 % indicate ion suppression while the values greater than 100% defines to ion enrichment [28]. For the investigation of matrix effect, 5 µg/L standard VAH solutions were spiked in three different water matrixes such as drinking water, seawater and wastewater. This effect is not an effect on the level that will cause problems in the measurements. The results about the recoveries and RSD (%) of VAHs spiked to drinking water, seawater and wastewater are shown in Table 7 and also, Figure 3. The values of RSD were determined ranging from 1.82 % to 5.47 % for drinking water, between 2.08 % to 6.78 % for seawater and over the range from 7.53 % to 10.08 % for wastewater. It is obvious that RSD range of wastewater is higher than RSD ranges of drinking water and seawater. Thus, it shows that there are no matrix effects in the drinking water and seawater. However, there is a matrix effect in wastewater at the level that can be neglected when compared with other matrices. A similar situation is seen in the recovery results of VAHs. In the study of matrix effect, there is a similar result obtained with the study of Hino and co-workers [19].

Table 7. Recoveries of VAHs spiked to drinking water, seawater and wastewater.

Compound	Drinking Water		Seawater		Wastewater	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Benzene	98.6	3.82	102.4	4.30	103.8	8.91
Toluene	102.4	3.81	109.0	3.22	108.9	10.08
Ethylbenzene	101.8	5.47	106.8	4.48	105.0	9.71
P&M-Xylene*	106.2	4.10	106.8	4.21	105.1	9.68
Styrene	89.0	4.89	85.8	6.78	104.6	10.08
O-Xylene	106.8	2.65	105.4	3.00	113.0	8.29
Isopropylbenzene	107.8	4.96	104.5	4.99	104.5	8.33
N-Propylbenzene	108.1	5.54	107.0	4.85	107.4	8.07
1,3,5-Trimethylbenzene	106.1	3.74	102.5	3.88	110.1	7.88
1,2,4-Trimethylbenzene	104.9	3.58	103.3	3.00	109.7	7.68
1,3-Dichlorobenzene	102.5	2.08	98.6	2.26	100.3	8.08
1,4-Dichlorobenzene	101.9	1.98	97.7	2.08	99.2	8.12
1,2-Dichlorobenzene	99.5	1.82	95.7	2.15	97.1	8.09
1,3,5-Trichlorobenzene	98.9	3.02	90.6	3.32	89.2	8.13
1,2,4-Trichlorobenzene	94.3	2.76	92.4	4.16	92.0	7.87
1,2,3-Trichlorobenzene	94.8	4.41	93.7	3.95	93.8	7.53

* Measurement of p&m-xylene was performed for 4 µg/L and 10 µg/L standard VAH solutions.

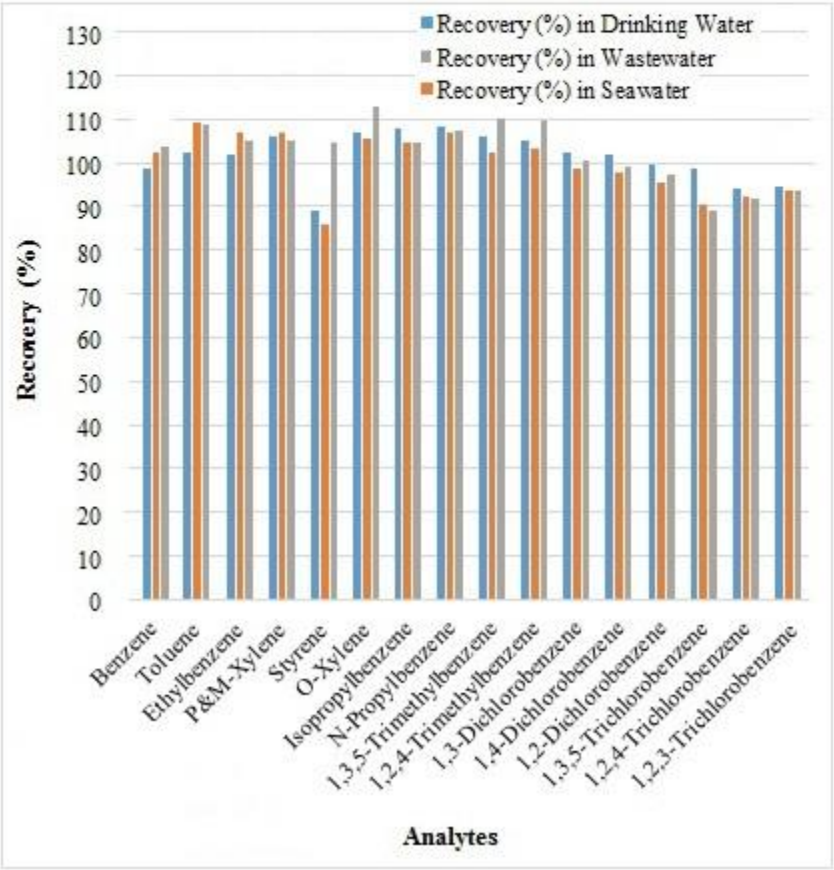

Figure 3. Evaluation of matrix effect for investigated VAHs in different water samples.

3.1.7. Real Samples

The developed analytical method was successfully applied to more than one hundred drinking water and wastewater and approximately fifty seawater samples sent to the laboratory for the analysis and quantification of VAHs. The results of the real samples containing VAHs and their observed concentration ranges are summarized in Table 8. The concentrations of identified analytes were computed in a six point's calibration curve by fitting its area ratio.

Table 8. VAHs and their observed concentration ranges in real samples.

Compound (µg/L)	Drinking Water	Seawater	Wastewater
Benzene	0.1-0.3	-	0.5-3.2
Toluene	-	-	0.1-6.2
Ethylbenzene	-	-	0.5-3.9
P&M-Xylene	-	-	0.4-2.6
Styrene	-	-	0.1-4.8
O-Xylene	-	-	0.4-3.7
Isopropylbenzene	-	-	0.1-0.3
N-Propylbenzene	-	-	-
1,3,5-Trimethylbenzene	-	0.1-0.5	0.2-1.4
1,2,4-Trimethylbenzene	0.1-0.2	0.1-0.7	0.3-0.5
1,3-Dichlorobenzene	-	-	-
1,4-Dichlorobenzene	-	0.1-1.4	0.4-1.2
1,2-Dichlorobenzene	-	-	-
1,3,5-Trichlorobenzene	-	0.1-0.5	-
1,2,4-Trichlorobenzene	-	0.1-0.3	0.1-0.3
1,2,3-Trichlorobenzene	0.1-0.2	0.1-07	0.2-1.1

4. CONCLUSION

New PT-GC-MS method was developed and validated for identification and quantification of sixteen VAHs in three different water matrices. The PT-GC, at which the volatile compounds was purged from the water sample by a stream of gases, adsorbed on a trap made of porous solid sorbents and desorbed into GC for separation and MS quantitation, has become a valuable and widely accepted method for the analysis of some VAHs in water [18]. Method development works were performed to utilize the studies in the literature in a comprehensive way. Validation studies of the method were performed according to EURACHEM guideline [21] and Guidelines for Standard Method Performance Requirements [25]. The characterization of proposed method was actualized and evaluated especially with respect to the recovery, reproducibility and repeatability. Mean recoveries of VAHs obtained at the end of the accuracy studies are quite gratifying ranging from 88.4 % to 94.6 % and the RSD results were found between 3.52 % and 6.35 %. The values of RSD in the intra-day study were found ranging from 1.76 % to 6.93 % and mean difference from two days ranged between 2.19 % to 5.92 % under the conditions for inter-day reproducibility. LOD values for VAHs was achieved from 0.01 to 0.02 µg/L, and the range of LOQ for VAHs was obtained from 0.02 to 0.08 µg/L. As can be seen from the results, all the investigated VAHs were successfully extracted and good accuracy, precision and low detection capabilities provide great convenience to the detection of investigated VAHs below the recommended analytical level in the related document/legislation [15, 19, 21, 25 27]. Based on these results, PT-GC-MS method indicated the availability for sensitive quantification of VAHs in water samples for water safety applications. Furthermore, the method has been tested by applying a large number of drinking water, seawater and wastewater. The most important features of proposed method are low sample preparation step and analysis time. This situation allows for the rapid and reliable analysis of a large number of samples in terms of VAHs.

Besides, the proposed method has been successfully used for the analysis of VAHs in different types of water samples over the last three years. In brief, the simplicity of this technique allows for the fast and accurate analysis of VAHs in different types of water samples.

Acknowledgment

This study was supported within the scope of Hazardous Waste Analysis Project situated in TUBITAK MAM Environment and Cleaner Production Institute. The authors wish to thank H. Demir, E. Ay and B. Kalay for their supports in the laboratory.

The authors have declared that there is no conflict of interest for the publication of this paper.

REFERENCES

[1]. Erol A., Ayla D., Mustafa Ö., Polisiklik Aromatik Hidrokarbonlar ve Sağlığa Etkileri, Mehmet Akif Üni. Fen Bil. Enst. Derg, 3-1 (2012) 45-52.

[2]. Tehrani R. and Van Aken B., Hydroxylated Polychlorinated Biphenyls in the Environment: Sources, Fate, and Toxicities, Environ. Sci. and Pollut. Res., 21-10 (2014) 6334-6345.

[3]. Tombs M.C., Volatile Organic Compounds in Water: Gas Chromatography, Encyclopaedia of Separation Science. North West Water Limited, Warrington, United Kingdom, 2000.

[4]. Jurdakova H., Kubinec R., Jurcisinova M., Krkosova Z., Blasko J., Ostrovsky I.,Sojak L., Berezkin V.G., Gas Chromatography Analysis of Benzene, Toluene, Ethylbenzene and Xylenes Using Newly Designed Needle Trap Device in Aqueous Samples, J. of Chrom. A, 1194 (2008) 161–164.

[5]. Bhattacharya S.S., Kim K.H., Ullah M.A., Goswami L., Sahariah B., Bhattacharyya P., The Effects of Composting Approaches on the Emissions of Anthropogenic Volatile Organic Compounds: A Comparison between Vermicomposting and General Aerobic Composting, Environ Pollut., 208 (2016) 600–607.

[6]. Mirzaei A., Leonardi S.G., Neri G., Detection of Hazardous Volatile Organic Compounds (VOCs) by Metal Oxide Nanostructures-Based Gas Sensors, A review Ceramics Inter., 42 (2016) 15119–15141.

[7]. Salar-García M.J., Ortiz-Martínez V.M., Hernández-Fernández F.J., de los Ríos A.P., Quesada-Medina J., Ionic Liquid Technology to Recover Volatile Organic Compounds (VOCs), J. of Hazard. Mater., 321 (2017) 484–499.

[8]. Kountouriotis A., Aleiferis P.G., Charalambides A.G., Science of the Total Environment Numerical Investigation of VOC Levels in the Area of Petrol Stations, Sci. of the Total Environ., 470 (2014) 1205–1224.

[9]. ASTM. The ASTM Standard Practice for Determining Volatile Organic Compounds (VOC) Contents of Paints and Related Coating (D3960), American Society for Testing and Materials, Philadelphia, USA, 1989.

[10]. Pettersson J. and Roeraade J., Method for Analysis of Polar Volatile Trace Components in Aqueous Samples by Gas Chromatography, Anal. Chem., 77 (2005) 3365-3371.

[11]. Demeestere K., Dewulf J., De Witte B., Van Langenhove H., Sample Preparation for the Analysis of Volatile Organic Compounds in Air and Water Matrices, J. of Chrom. A, 1153 (2007) 130–144.

[12]. Ikem A., Measurement of Volatile Organic Compounds in Bottled and Tap Waters by Purge and Trap GC–MS: Are Drinking Water Types Different?, J. of Food Comp. and Anal., 23 (2010) 70–77.

[13]. Wang A., Fang F., Pawliszyn J., Sampling and Determination of Volatile Organic Compounds with Needle Trap Devices, J. of Chrom. A, 1072 (2005) 127–135.

[14]. Chary N.S. and Fernandez-Alba A.R., Determination of Volatile Organic Compounds in Drinking and Environmental Waters, Trends in Anal. Chem., 32 (2012) 60–75.

[15]. Ueta I., Mitsumori T., Suzuki Y., Kawakubo S., Saito Y., Determination of Very Volatile Organic Compounds in Water Samples by Purge And Trap Analysis with A Needle-Type Extraction Device, J. of Chrom. A, 1397 (2015) 27–31.

[16]. Chen P.S., Tseng Y.H., Chuang Y.L., Chen J.H., Determination of Volatile Organic Compounds in Water Using Headspace Knotted Hollow Fiber Microextraction, J. of Chrom. A, 1395 (2015) 41–47.

[17]. Silgoner I., Rosenberg E., Grasserbauer M., Determination of Volatile Organic Compounds in Water by Purge-And-Trap Gas Chromatography Coupled to Atomic Emission Detection, J. of Chrom. A, 768 (1997) 259–270.

[18]. Wu Z. and Fung Y.S., Isolation and Determination of Volatile Organic Compounds from Water by Dynamic Purge-and-Trap Technique Coupled with Capillary Gas Chromatography, Inter. J. of Environ. Anal. Chem., 82 (2010) 431-442.

[19]. Hino T., Nakanishi S., Maeda T., Hobo T., Determination of Very Volatile Organic Compounds in Environmental Water by Injection of a Large Amount of Headspace Gas into a Gas Chromatograph, J. of Chrom. A, 810 (1998) 141–147.

[20]. EPA. Method 524.3: Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Version 1.0, 2009.

[21]. EURACHEM. The Fitness for Purpose of Analytical Methods: A Laboratory Guide to Method Validation and Related Topics, 2nd edition, LGC, Teddington, 2014.

[22]. ATSDR. Agency for Toxic Substances and Registry, U.S. Public Health Service, U.S. Department of Health and Human Service, Atlanta, 1997.

[23]. EPA. Volatile Organic Compounds in Water, Soil, Soil gas, and Air by Direct Sampling Ion Trap Mass Spectrometry (DSITMS), U.S. Public Health Service, U.S. Department of Health and Human Service, USA, 2002.

[24]. Alonso M., Cerdan L., Godayol A., Antico E., Sanchez J.M., Headspace Needle-Trap Analysis of Priority Volatile Organic Compounds from Aqueous Samples: Application to the Analysis of Natural and Wastewaters, J. of Chrom. A, 1218 (2011) 8131-8139.

[25]. AOAC. Guidelines for Standard Method Performance Requirements, Appendix F., Association of Analytical Chemists, 20th edition, vol. 2, 2016,

[26]. Saito Y., Ueta I., Kotera K., Ogawa M., Wada H., Jinno K., In-Needle Extraction Device Designed For Gas Chromatographic Analysis Of Volatile Organic Compounds, J. of Chrom. A, 1106 (2006) 190-195.

[27]. Shin H.S. and Kim T.S., Analysis of Tert-Butanol, Methyl Tert-Butyl Ether, Benzene, Toluene, Ethylbenzene and Xylene in Ground Water by Headspace Gas Chromatography-Mass Spectrometry, Bull. Korean Chem. Soc., 30-12 (2009) 3049-3052.

[28]. Kaplan M., Oktem-Olgun E., Karaoglu O., A Rapid and Simple Method for Simultaneous Determination of Triphenylmethane Dye Residues in Rainbow Trouts by Liquid Chromatography–Tandem Mass Spectrometry, J. of Chrom. A, 1349 (2014) 37–43.