Method validation and measurement uncertainty of possible thirty volatile organic compounds (VOCs) presented in the polyethylene present in bottled drinking waters sold in Turkey

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Abstract

This study was actualized for the simultaneous determination of possible thirty VOCs presented in drinking waters in Turkey by direct injection to purge and trap (PT) gas chromatography-mass spectrometry (GC-MS). It consists of selectivity, linearity, the limit of detection (LOD) and limit of quantification (LOQ), accuracy (recovery), precision, trueness, and measurement uncertainty studies. In linearity, the values of correlation coefficients (r^2) for the matrix-matched calibration curves were higher than 0.998 for all analytes. This method showed high sensitivity (LOD: 0.011–0.040 µg/L; LOQ: 0.035–0.133 µg/L), quite sufficient recovery (82.6% to 103.1%) for accuracy, and acceptable precision (intra-day recovery: 81.5–104.4%, relative standard deviation (RSD): 1.04–9.81%; inter-day recovery: 92.6–104.1%, RSD: 1.15–7.52%). All the recovery and RSD values obtained below 10% are evaluated agreeable in point of the AOAC and EURACHEM/CITAC validation guidelines. The recovery percentages of all analytes in CRM changed between 80.3 and 109.9% and the RSD (%) values for each analyte obtained below 10%. The proficiency test results were satisfactory and comparable (z score less than or equal to 2.0 is no questionable or satisfactory) to those obtained by other laboratories participating in the round. The calculated percentage of relative uncertainties for each analyte changed from 2.99 to 10.10% and the major contribution to uncertainty budget arises from the calibration curve and repeatability. Therefore, the results demonstrate that this method is applicable for the determination of possible thirty VOCs in drinking waters in routine analysis for custom laboratories.

Keywords: Drinking water, Gas chromatography, Measurement uncertainty, Method validation, Purge and trap, Volatile organic compounds (VOCs)

Introduction

Global warming caused by the increase in greenhouse gas emissions and increasing urbanization and industrialization activities has adverse effects on water and water resources such as drought. Nowadays, this situation is reaching much serious level in terms of threating the quality of human life. Therefore, protection from all kinds of pollution and more

efficient use of existing water resources are of vital importance for human health (Dehghani Darmian et al. 2018). The presence of chemical substances in the water environment causes many diseases and health problems such as cancer, liver, and kidney diseases (Tehrani and Van Aken 2014). Various regulations have been published at national and international levels regarding the protection of water such as European Union (EU) Water Framework Directive (2000/60/EC), Drinking Water Directive (98/83/EC), Prevention and Control Regulation (PCR), the Food and Environmental

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Protection Act (FEPA/1985), the Control of Pesticides Regulations (COPR/1986), and the United Kingdom (UK) Surface Waters (dangerous substances) Regulations (SI 1997/2560). These regulations ensure that water is continuously monitored and kept under control (Tombs 2000).

Volatile organic compounds (VOCs) have been one of the most studied organic pollutant class in recent years due to its persistent and toxic effects on human health. For example, methylbenzene (toluene), dichlorobenzenes, trichlorobenzenes, dimethyl benzenes (xylenes), tetrachloromethane, dibromochloromethane, and trichloroethene are persistent organic substances for the environment and human life (Tombs 2000; Jurdakova et al. 2008; Bhattacharya et al. 2016; Mirzaei et al. 2016). They are composed of carbon chains and possess high vapor pressure at room temperature (Kountouriotis et al. 2014). The American Society for Testing and Materials (ASTM) has stated in pursuant of D3960 test method that VOCs have higher vapor pressure than 0.1 mmHg (Table 1) at 25 °C (ASTM 1989). Their boiling points change between 40 and 260 °C (Güzel et al. 2018). Besides, World Health Organization (WHO) describes compounds with boiling point of 50 °C to 100 °C as very volatile organic compounds (VVOC) (WHO 1987). High vapor pressure (low boiling point) of VOCs allows greater number of molecules to move freely and causes the substance to change form quickly. This allows the substances to spread easily into the environment. For this reason, they can make carcinogenic, mutagenic, and toxic effects by easily reaching people (Tsuchiya 2010). Hence, they need to analyze their species and amounts, especially in water in order to reduce the toxic effects of human life.

Analytical chemistry and food laboratories need to sensitive and reliable methods more than ever to obtain practicable qualitative and quantitative data. Recently, chemical analysis has been taken into consideration as the main approach for the detection of VOCs and similar organic pollutants in water samples. Because of their toxicity and persistence, today, an analytical method is required to determine trace amounts in the water matrix. For this purpose, this study was to validate a fully automated analytical method for the determination of thirty water-soluble VOCs in drinking water samples using purge and trap (PT) gas chromatography-mass spectrometry (GC-MS) system. Conventional measurement methods include pretreatment stage to concentrate the sample before analysis. These pre-treatments require a long period of time and are costly due to the use of solvents. In contrast to these methods, the proposed method is completely automatic and does not include an additional pre-treatment step and solvent use. The sample has been concentrated by PT system. This study especially provides saving on time and reduces the cost of analysis. The method, that has been optimized and has

been identified measurement uncertainty limits in detail, contributes rapid, simple, sensitive, and accurate qualification and quantification of possible thirty VOCs in drinking water samples at the same time.

Materials and methods

The studies of this research were carried out in the Scientific and Technological Research Council of TURKEY Marmara Research Center (TUBITAK MAM) Environment and Cleaner Production Institute laboratories. They possess national accreditation certificate taken from Turkish Accreditation Agency (TURKAK) pursuant to TS EN ISO/IEC 17025:2012 standard since July 16, 2010, and "Environmental Measurement and Analysis Qualification Certificate" from the Republic of Turkey Ministry of Environment and Urbanization acquired on February 21, 2011, respectively. Besides, they have international accreditation certificates acquired from German Accreditation Council DAR/DAP (Deutscher Akkreditierung Rat) between December 17, 2002 and 2010.

Reagents and chemicals

Ampoule of VOC standard solution containing 60 different chemicals (200 mg/L each in methanol) was purchased from High-Purity Standards Co., Inc. (North Charleston, USA). Standard solution of 1,2,3-trichlorobenzene in methanol (GC gradient grade) with purities higher than 99.8% was supplied by Dr. Ehrenstrofer (Augsburg, Germany). 4-Bromofluorobenzene (25 mg/mL in methanol), which is used as the internal standard (IS) in the analysis, was purchased from Absolute Standards Co., Inc. (Hamden, USA). The highest purity grade methanol was obtained from Merck (Darmstadt, Germany) and the purification of water was performed with Milli-Q Plus system (EMD Millipore, Billerica, MA).

Further, 1 mg/L and 10 mg/L concentrations of stock standard solutions were prepared by mixing 200 mg/L stock VOC solution and 100 mg/L 1,2,3-trichlorobenzene. These solutions were stored in a freezer (− 20 °C) at 1.5 mL vials. They should be prepared again once a month because of their stability. Standard solutions were made ready for the linearity and other studies by dilution of stock standard solutions in the ultra-purified water.

Water samples

Commercial one hundred drinking water samples sold in grocery markets and supermarkets in Turkey were supplied used in the study. They were preserved and handled in accordance with the related International Organization for Standardization (ISO) standard (ISO 2012). The analysis of whole samples (stored at less than 5 °C) was carried out within 48 h after they were purchased.

Table 1 Some physical, chemical, and GC-MS properties of VOCs (ATSDR 1997; EPA 2002; Alonso et al. 2011; Güzel et al. 2018)

Compound	Boiling point (°C)	Vapor pressure (mm Hg)	Density (g/cm³)	Retention time (min)	Target ion (m/z)	Quantified ion (m/z)
Dichloromethane	40	58.4 (25 °C)	1.33	5.38	86	84
1,1-Dichloroethane	57	180.0 (20 °C)	1.24	5.95	63	65
Trichloromethane	61	158.3 (20 °C)	1.48	6.74	83	85
1,2-Dichloroethane	84	61.0 (20 °C)	1.25	7.40	62	64
Benzene	80	95.2 (25 °C)	0.88	7.62	77	78
Trichloroethene	87	58.0 (20 °C)	1.46	8.68	95	130
Bromodichloromethane	90	50.1 (20 °C)	1.90	9.10	83	85
Toluene	111	28.4 (25 °C)	0.87	10.90	91	92
Dibromochloromethane	119–120	5.5 (25 °C)	2.38	12.14	127	129
Tetrachloroethene	121	12.8 (20 °C)	1.62	12.26	166	164
Tetrachloromethane	77	91.3 (20 °C)	1.59	13.86	117	118
1,1,1,2-Tetrachloroethane	131	12.0 (25 °C)	1.54	13.91	131	133
Ethylbenzene	136	6.8 (20 °C)	0.90	14.17	91	106
P&M-Xylene	138–139	8.8 (25 °C)	0.86	14.47	91	106
Styrene	145	4.5 (20 °C)	0.91	15.21	91	103
O-Xylene	144	6.7 (25 °C)	0.88	15.25	91	106
Tribromomethane	149	5.3 (20 °C)	2.89	15.30	173	171
1,1,2,2-Tetrachloroethane	147	5.7 (25 °C)	1.59	16.12	83	85
4-Bromofluorobenzene (IS)	152	4.1 (25 °C)	1.50	16.20	95	174
Isopropylbenzene	151	4.5 (25 °C)	0.86	16.25	105	120
N-Propylbenzene	159	3.4 (25 °C)	0.86	17.18	91	120
1,3,5-Trimethylbenzene	165	1.9 (20 °C)	0.86	17.68	105	120
1,2,4-Trimethylbenzene	168	7.0 (44 °C)	0.88	18.45	105	120
1,3-Dichlorobenzene	173	3.4 (38 °C)	1.29	18.87	146	148
1,4-Dichlorobenzene	174	2.2 (25 °C)	1.25	19.14	146	148
1,2-Dichlorobenzene	180	1.7 (25 °C)	1.30	19.70	146	148
1,3,5-Trichlorobenzene	208	1.4 (25 °C)	1.46	22.40	180	182
1,2,4-Trichlorobenzene	214	10.0 (78 °C)	1.45	23.59	180	182
Naphthalene	218	0.1 (25 °C)	1.16	23.90	128	51
Hexachloro-1,3-butadiene	215	0.2 (25 °C)	1.56	24.35	225	223
1,2,3-Trichlorobenzene	218	1.0 (25 °C)	1.45	24.44	180	182

Analytical instrumentation

PT analytical condition

PT system used for the extraction and enrichment of investigated VOCs from samples was an OI Analytical Eclipse model 4660 sample concentrator (College Station, TX, USA) equipped with an OI Analytical 4552 water/soil autosampler. The sample was added into 50 mL PT glass vial until filled and then, 25 mL of sample was transferred to the purge unit, which is the extraction cell of the analytes in the sample. The IS (20 μL from IS with a concentration of 2.5 mg/L) was added to the sample via injector before purge process. To extract all the volatile analytes wholly, a sample was purged with the help of pure helium gas (purge gas). At the end of the purging process, analytes were sent to the trap unit (trapping material is Purge Trap K VOCARB 3000). Consequently, collected analytes in the trap were transferred to GC column for the separation by desorbing via high temperature. The PT system was programmed as follows: purge-ready temperature: 35 °C, purge time: 11 min, dry purge time: 5 min, purge gas flow rate: 50 mL/min, desorb preheat: 180 °C, desorb time: 1 min, desorb temperature: 180 °C, bake time: 7 min, bake temperature: 260 °C.

GC-MS analytical condition

The analyses for the determination and quantification of thirty VOCs were actualized by using Agilent Technologies 6890N Network GC system (Avondale, USA)

coupled with a 5975C inert mass spectrometer with a triple detector (MSD). The separations were performed using a DB-5ms fused silica capillary column as an analytical column in GC separation having 60 m × 0.25 μm with a 0.25 μm film thickness (Agilent Technologies J&W Scientific, Folsom, CA, USA) and the injector temperature was set to 200 ℃. The split mode for all analysis was used with a ratio of 20:1 by using a 4.0 mm split liner at 200 ℃. The helium of 99.9995% purity at a gas flow rate of 1.0 mL/min was employed as the carrier gas with a pressure of 110 kPa in the port of injection. The adjustment of initial temperature and ionization voltage of GC system was adjusted to 280 ℃ and 70 eV by selecting electron impact ionization (EI-SIM). At the beginning of the analysis, the column temperature of GC system was programmed to 40 ℃ for 2 min and was run to increase to 200 ℃ at a rate of 7 ℃/min. When the GC system arrived at the final temperature, it was held for 5 min. The MS was arranged to a total-ion-monitoring mode (m/z: 25–550). The confirmation of each compound was realized with two MS characteristic ions; the ratio of two MS characteristic ions and GC retention times matches to the known standard compounds. The confirmation and quantification of each VOC were shown in Table 1 with relevant target and quantified ions. The optimum performance values of GC-MS and PT systems mentioned above for the analysis of related VOCs in water were determined in consequence of experimental works carried out before the validation study of these parameters.

Results and discussion
Method optimization study
Optimization of PT condition
PT is a sample pre-treatment system that allows the collection of VOCs in the sample simply with high precision and efficiency. In PT system, VOCs found in water are transported by boiling efficiently to the vapor phase and they are passed through an absorbent trap with the aid of the purge gas such as helium. After purging process has finished, the trap containing VOCs is heated to deliver a gas chromatographic column and VOCs along with heating are delivered with the carrier gas. At this stage, the parameters of purge time, purge gas flow rate, and desorb temperature play vital role for the most effective collection of VOCs from the sample.

In the determination of VOCs, purge gas flow rate and purge have a crucial importance for the efficiency of the trap and analysis time. The high flow rate brings about both failure to capture VOCs by the trap and low MS sensitivity and troubled drying because of blowing-out of water. Besides, the low flow rate affects the collection of VOCs from the sample per unit time and leads to prolonged analysis time (Hong-Hai et al. 2015). Thus, the

optimum value of the flow rate of purge gas must be determined to actualize the accurate and sensitive analysis. Measurements at different flow rates with parallel study (*n* = 4) were performed for 5 μg/L standard solution at a certain purge time. Figure 1a presents the relationship between flow rate of purge gas and related peak area. The results demonstrated that 40 mL/min of purge gas flow with regard to the high purge efficiency was found optimum for almost all of VOCs with negligible exceptions such as trichloromethane, tetrachloromethane, isopropylbenzene, 1,2,4-trichlorobenzene, and naphthalene. After establishing the optimum value of the purge gas flow rate, the purge time was determined. Measurements with different purge times (8, 9, 10, 11, 12, and 13 min) were carried out for 5 μg/L standard solution at the purge gas flow rate of 40 mL/min. Fig. 1b shows the dealings between purge time of instrument and peak area of VOCs. When the peak areas of VOCs in the sample were examined, the results revealed that purge time of 11 min is more than enough to get the best results. Exposing the sample to a longer purge time will not cause any appreciable change in results. It prolongs the analysis time and leads to unnecessary gas consumption. Thus, 11 min was decided as fittest purge time in real work.

At the end of purging of VOCs in sample, VOCs retained in trap, which allows the purge gas to pass through to vent, were then desorbed by heating the trap at a suitable desorb temperature. Because, overheating the trap may cause decomposition of the compounds and adsorbent material. Therefore, the optimization of desorb temperature was actualized in this work. Measurements went through with 5 μg/L standard solution at the purge time of 11 min and at the purge flow rate of 40 mL/min. The results in Fig. 1c exhibited that almost whole of VOCs in sample was collected from the trap at 180 ℃ of desorb temperature, which was found optimum.

Method verification study
The performance of proposed method was evaluated with regard to selectivity, linearity, the limit of detection (LOD) and quantification (LOQ), trueness, accuracy, and precision in accordance with Commission Decision EURACHEM Guideline (EURACHEM/CITAC 2014) and Guidelines for Standard Method Performance Requirements (AOAC 2016). Water having high purity was used as a blank sample.

Selectivity
The selectivity study of the method was carried out by the analyses of seven drinking water samples to control the stability of retention times and the ratio of target and quantified ion signals of each analytes. In
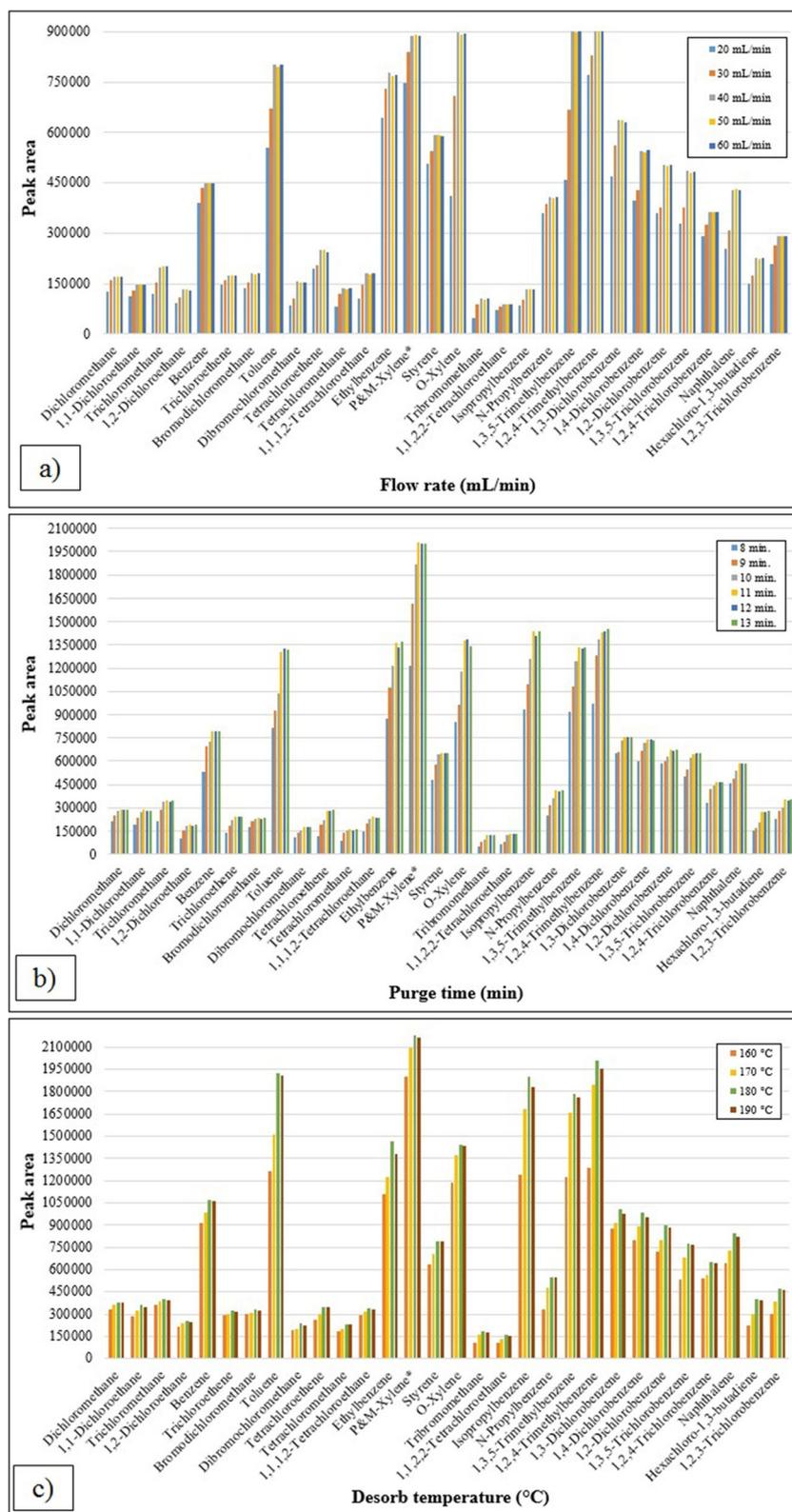
Fig. 1 Effect of **a)** purge gas flow rate, **b)** purge time, and **c)** desorb temperature on analytical measurements

consequence of GC-MS analyses of these samples, the results indicated that there are no peaks of interfering compounds that will cause positive results in the analysis.

Linearity

For the evaluation of linearity of the calibration curve, matrix-match calibration curves of spiked drinking water samples were employed. The calibration curves for each VOCs were prepared at nine (0.15 μg/L, 0.25 μg/L, 0.5 μg/L, 1 μg/L, 2 μg/L, 5 μg/L, 10 μg/L, 20 μg/L, and 40 μg/L) concentration levels (Fig. 2) spiked from two stock standard solutions(1 mg/L and 10 mg/L) by paying regard to their signal intensities. The values of correlation coefficient (r^2), calibration curve equation ($y = ax + b$) and dynamic linear range from all calibration curves are illustrated in Table 2. In a similar study, Ferreira et al. (2016) presented that the linear regression with correlation coefficient should be equal or better than 0.99 (good linearity) for the evaluation of the linearity range. In the light of this approach, the values of correlation coefficients for the matrix-matched calibration curves were higher than 0.998 for all analytes in this study. The analytical response linearity in the working concentration range can be assessed as a great in pursuance of correlation coefficients. The dynamic linear range was determined from 0.15 to 20 μg/L for the majority of the studied VOCs except for dichloromethane, toluene, and p&m-xylene.

LOD and LOQ

The evaluation of method sensitivity has been done with the determination of LOD and LOQ values. Figure 3 shows the chromatogram of 5 μg/L standard solution, which is used for the determination LOD and LOQ levels of VOCs. The LOD and LOQ were calculated as (Eq. (1) and Eq. (2)):

$$LOD = \frac{3\sigma}{S} \tag{1}$$

and,

$$LOD = \frac{10\sigma}{S} \tag{2}$$

where σ is the standard deviation and S is the slope of the standard curve.

The calculations of LOD and LOQ results were made from the mean noise value in the chromatogram. The results of LOD and LOQ are given in Table 3. Thus, LOD values for all VOCs were found to be in the range of 0.011 μg/L and 0.040 μg/L, and the ranges of LOQ for VOCs were obtained from 0.035 to 0.133 μg/L. The LOD and LOQ values presented in this work are similar to LODs and LOQs reported for VOCs analysis in drinking water samples and similar types of water samples developed for Jurdakova et al. (2008), Chary and Fernandez-Alba (2012), and Ueta et al. (2013). Moreover, The LOD and LOQ values of some VOCs studied in this work are less than the values obtained in the other studies (Kubinec et al. 2004; Alonso et al. 2011; Chen et al. 2015) in literature for the analysis of VOCs in water samples.
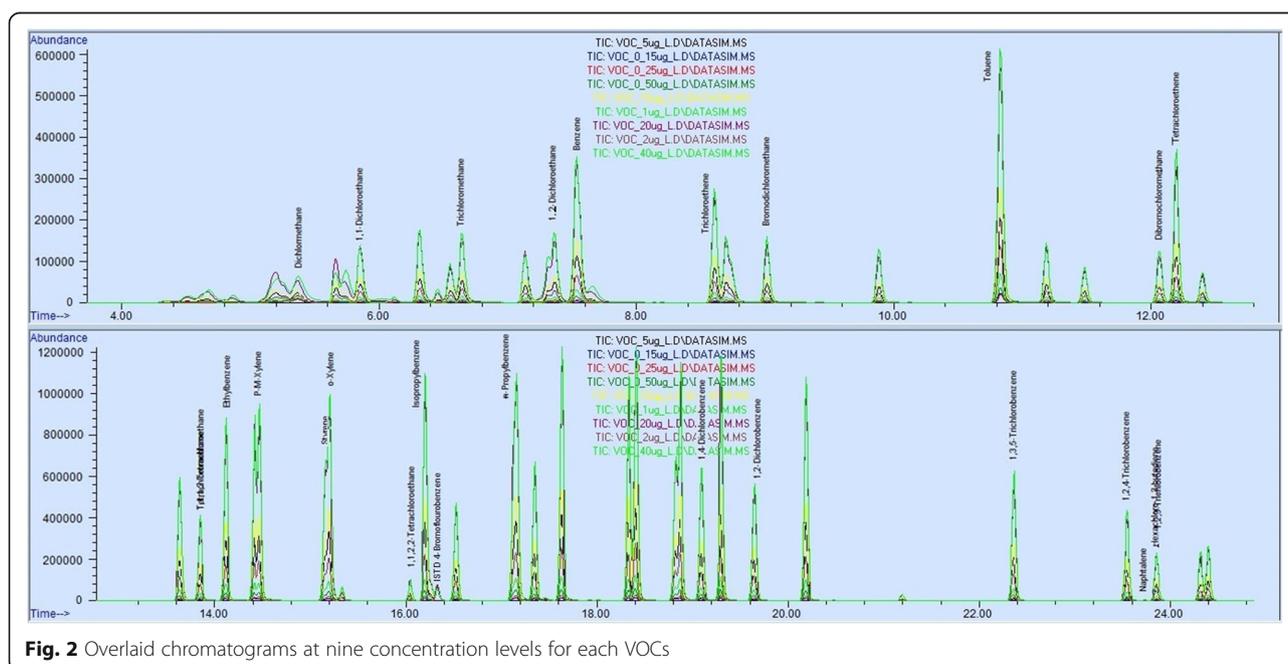

Fig. 2 Overlaid chromatograms at nine concentration levels for each VOCs

Table 2 Linearity, LODs, LOQs, and accuracy study of VOCs

Compound	Coefficient correlation (r^2)	Calibration curve equation ($y = ax + b$)	Linear dynamic range (µg/L)	LOD (µg/L)	LOQ (µg/L)	Mean recovery (%)	RSD (%)
Dichloromethane	0.9991	$y = 18054x + 213661$	2.00–20.00	0.024	0.079	88.9	4.62
1,1-Dichloroethane	0.9998	$y = 32546x - 500.11$	0.15–20.00	0.023	0.076	92.7	7.17
Trichloromethane	0.9998	$y = 34184x - 5046.6$	0.15–20.00	0.019	0.063	95.1	4.16
1,2-Dichloroethane	0.9996	$y = 13031x - 2191.5$	0.15–20.00	0.036	0.120	93.3	2.65
Benzene	0.9997	$y = 75303x + 9609.7$	0.15–20.00	0.019	0.065	92.5	5.69
Trichloroethene	0.9990	$y = 24918x - 6931.5$	0.15–20.00	0.027	0.091	91.9	7.86
Bromodichloromethane	0.9988	$y = 20290x - 8183.6$	0.15–20.00	0.029	0.097	90.7	2.97
Toluene	0.9996	$y = 97609x + 97944$	0.25–20.00	0.017	0.058	94.0	6.14
Dibromochloromethane	0.9983	$y = 10346x - 5086.4$	0.15–20.00	0.039	0.130	88.9	3.41
Tetrachloroethene	0.9999	$y = 22962x - 363.87$	0.15–20.00	0.024	0.080	87.2	7.91
Tetrachloromethane	0.9993	$y = 12673x - 3735.9$	0.15–20.00	0.021	0.071	94.6	2.48
1,1,1,2-Tetrachloroethane	0.9993	$y = 17912x - 5135$	0.15–20.00	0.028	0.093	88.1	3.66
Ethylbenzene	0.9999	$y = 121781x + 6841.1$	0.15-20.00	0.015	0.050	92.7	6.17
P&M-Xylene[a]	0.9997	$y = 44856x - 9081.3$	0.30–40.00	0.011	0.037	95.1	7.14
Styrene	0.9999	$y = 57766x - 10087$	0.15–20.00	0.014	0.047	82.6	3.29
O-Xylene	0.9998	$y = 93040x - 2895.5$	0.15–20.00	0.021	0.071	95.9	4.58
Tribromomethane	0.9989	$y = 4559.6x - 1681.6$	0.15–20.00	0.035	0.116	89.4	3.19
1,1,2,2-Tetrachloroethane	0.9995	$y = 8716.6x - 2753.5$	0.15–20.00	0.040	0.133	91.3	2.65
Isopropylbenzene	0.9996	$y = 133550x + 18469$	0.15–20.00	0.012	0.038	91.9	6.98
N-Propylbenzene	0.9998	$y = 236680x + 35492$	0.15–20.00	0.016	0.054	94.3	7.83
1,3,5-Trimethylbenzene	0.9999	$y = 112267x + 11792$	0.15–20.00	0.016	0.056	95.0	7.24
1,2,4-Trimethylbenzene	0.9998	$y = 107730x + 14524$	0.15–20.00	0.015	0.045	97.4	5.65
1,3-Dichlorobenzene	0.9996	$y = 44536x - 5264.9$	0.15–20.00	0.013	0.043	98.6	3.04
1,4-Dichlorobenzene	0.9996	$y = 39184x - 2500.3$	0.15–20.00	0.019	0.061	99.2	3.71
1,2-Dichlorobenzene	0.9999	$y = 31839x - 3378.3$	0.15–20.00	0.011	0.035	98.4	2.61
1,3,5-Trichlorobenzene	0.9999	$y = 31299x + 168.14$	0.15–20.00	0.012	0.041	97.1	4.98
1,2,4-Trichlorobenzene	0.9999	$y = 17134x - 2202.7$	0.15–20.00	0.014	0.047	96.6	4.01
Naphthalene	0.9997	$y = 17499x - 5484.5$	0.15–20.00	0.012	0.040	95.3	5.22
Hexachloro-1,3-butadiene	0.9994	$y = 16910x + 2436.6$	0.15–20.00	0.025	0.083	93.8	9.19
1,2,3-Trichlorobenzene	0.9997	$y = 9467.3x - 894.31$	0.15–20.00	0.021	0.069	103.1	4.51

[a]In accuracy study, measurements of p&m-xylene were performed for 2 µg/L, 4 µg/L and 10 µg/L standard solutions
RSD: relative standard deviation

The accuracy of the method

The reliability of the method was confirmed by recovery experiments performed in the drinking water sample spiked with three different concentrations of 1 µg/L, 2 µg/L, and 5 µg/L for VOCs and seven measurements were carried out for each spiked concentration level. The recovery of each analyte at each concentration level was calculated by using Eq. (3):

$$\text{Analyte recovery}(\%) = \frac{\text{Determined concentration of analyte}}{\text{Spiked concentration of analyte}} x100$$

(3)

The percentage of mean recovery and the relevant RSDs for each VOC recovery at each spiked concentration level were depicted in Table 2. The recoveries ranged from 82.6 to 103.1%. The percentage of RSD values for VOCs changed between 2.48 and 9.19. These results demonstrate that this method has considerably
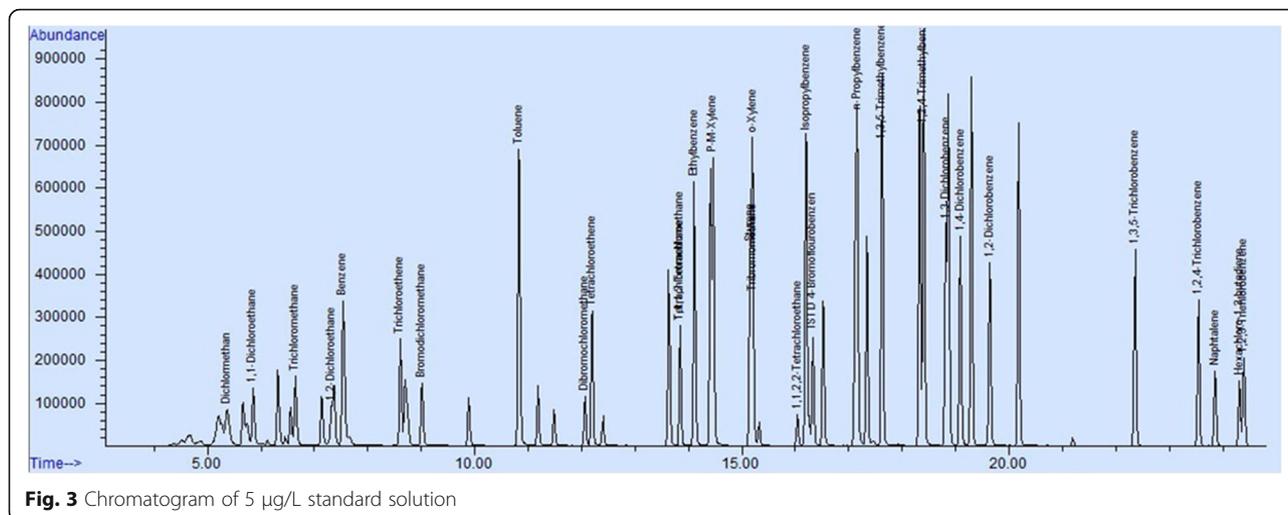
Fig. 3 Chromatogram of 5 μg/L standard solution

good and sufficient capability for the accurate analysis of VOCs in water. As can be seen, the accuracy results of the method were satisfied and verified with validation guideline for Standard Method Performance Requirements (AOAC 2016). Besides, Wu and Fung (2010) for BTEX (benzene, toluene, ethylbenzene, xylenes) (94.7–99.1%) and Ueta et al. (2013) for BTEX and THMs (trihalomethanes) (97.6–103.9%) reported similar recoveries.

The precision of the method

The precision of the method was calculated as RSD and was assessed as intra-day and inter-day precision. Within the scope of intra-day precision (repeatability), six drinking water samples were spiked with VOCs at each fortification level (2 μg/L and 5 μg/L) on the same day. The inter-day precision (reproducibility) study was done by injecting each of 5 μg/L concentrations of standard solution six times in different days in drinking water sample. The chromatograms of precision study were shown in Fig. 4. As can be seen in Table 3, RSD values for 2 μg/L and 5 μg/L concentration levels in intra-day precision were in the range of 1.04% to 9.81% and 1.67% to 7.04%, respectively. RSD values for 5 μg/L concentration levels in inter-day precision changed between 1.40 and 7.52%. All the RSD values obtained below 10% are considered acceptable for this parameter in accordance with the validation guideline (AOAC 2016).

Trueness

The performance of a method is measured by evaluating with regard to the precision and trueness. From this perspective, trueness refers to how close the average result (obtained from the method) of a series of studies is to the actual value (EURACHEM/CITAC 2014). The trueness of analytes in this study was checked with

PriorityPollutnT QC 710 coded certified reference material (CRM) issued from ERA-A Waters Company. The results of relevant CRM measured by PT-GC/MS system are presented in Table 4. The recovery percentages of all analytes changed between 80.3 and 109.9% and the RSD (%) values for each analyte obtained below 10%. These results are favorable according to the relevant verification guidelines (EURACHEM/CITAC 2012; EURACHEM/CITAC 2015).

The proficiency test is an important study to evaluate the validity of verified analysis methods of all the laboratories. It is also performed to ensure an objective assessment of the accuracy and reliability of laboratory calibration, test, and analysis results. Therefore, the proposed method was applied in the proficiency test for each VOCs studied in water matrix to evaluate the validation of the method. The results obtained from the proficiency test are given in Table 4. It was evaluated laboratory performance based upon the z score, which was calculated as (Eq. (4)):

$$z = \frac{(x - X)}{\text{SDPA}} \tag{4}$$

where x is the laboratory reported value and X is the assigned value, determined by formulation or robust mean and SDPA is the standard deviation for proficiency assessment on a fixed percentage.

The obtained z scores in the test may be categorized in accordance with the literature (Camino-Sánchez et al. 2013) as follows: (a) z score less than or equal to 2.0 is no questionable or satisfactory; (b) z score greater than 2.0 and less than 3.0 is warning; and (c) z score greater than or equal to 3.0 is unsatisfactory. As a result, the validity of the method was proved by the fact that the

Table 3 Intra and inter-day precision results of VOCs

Compound	Intra-day (repeatability)						Inter-day (reproducibility)					
	2 µg/L (n = 6)			5 µg/L (n = 6)			Day 1 (5 µg/L (n = 6))			Day 2 (5 µg/L (n = 6))		
	Measured (µg/L)	Recovery (%)	RSD (%)	Measured (µg/L)	Recovery (%)	RSD (%)	Measured (µg/L)	Recovery (%)	RSD (%)	Measured (µg/L)	Recovery (%)	RSD (%)
Dichloromethane	1.94 ± 0.05	95.7	2.55	4.24 ± 0.18	84.7	4.27	5.04 ± 0.19	100.9	3.81	4.92 ± 0.17	98.3	3.40
1,1-Dichloroethane	1.86 ± 0.09	93.0	4.73	4.92 ± 0.28	98.3	5.74	5.16 ± 0.18	103.2	3.47	5.01 ± 0.19	100.3	3.80
Trichloromethane	1.97 ± 0.07	98.7	3.41	4.54 ± 0.08	90.8	1.67	4.95 ± 0.11	98.9	2.27	5.10 ± 0.11	102.0	2.07
1,2-Dichloroethane	1.99 ± 0.05	99.4	2.34	4.41 ± 0.11	88.2	2.60	4.88 ± 0.12	97.5	2.44	4.78 ± 0.10	95.6	1.92
Benzene	1.89 ± 0.08	94.5	4.13	4.75 ± 0.09	94.9	1.85	4.89 ± 0.12	97.7	2.41	4.76 ± 0.17	95.2	3.46
Trichloroethene	2.02 ± 0.11	101.0	5.27	4.75 ± 0.11	95.1	2.28	5.06 ± 0.19	101.3	3.83	5.05 ± 0.29	101.0	5.75
Bromodichloromethane	1.89 ± 0.04	94.5	2.09	4.34 ± 0.11	86.7	2.67	5.09 ± 0.13	101.9	3.12	5.00 ± 0.09	100.1	1.72
Toluene	1.99 ± 0.09	99.4	4.50	4.65 ± 0.09	93.0	1.90	4.83 ± 0.25	96.6	5.10	4.92 ± 0.26	98.4	5.36
Dibromochloromethane	1.84 ± 0.02	92.1	1.19	4.38 ± 0.17	87.5	3.97	5.05 ± 0.12	101.0	2.35	4.93 ± 0.13	98.7	2.63
Tetrachloroethene	1.97 ± 0.19	98.5	9.81	4.20 ± 0.15	83.9	3.51	5.09 ± 0.35	101.9	6.79	5.03 ± 0.29	100.5	5.78
Tetrachloromethane	1.99 ± 0.03	99.4	1.52	4.72 ± 0.12	94.3	2.54	4.91 ± 0.31	98.1	6.25	4.95 ± 0.12	99.1	2.46
1,1,1,2-Tetrachloroethane	1.87 ± 0.04	93.4	2.11	4.32 ± 0.08	86.5	1.77	5.02 ± 0.15	100.4	2.92	4.91 ± 0.12	98.2	2.36
Ethylbenzene	1.97 ± 0.11	98.4	5.38	4.74 ± 0.08	94.8	1.76	4.78 ± 0.25	95.6	5.13	4.84 ± 0.11	96.9	2.32
P&M-Xylene[a]	4.01 ± 0.20	100.3	4.98	9.47 ± 0.17	94.7	1.78	9.87 ± 0.58	98.7	5.85	10.13 ± 0.66	101.3	6.75
Styrene	1.63 ± 0.03	81.5	1.94	4.36 ± 0.09	87.1	2.14	4.84 ± 0.12	96.9	2.45	4.88 ± 0.09	97.7	1.93
O-Xylene	2.01 ± 0.07	100.7	3.60	4.76 ± 0.17	95.1	3.49	4.77 ± 0.14	95.5	2.98	4.86 ± 0.05	97.2	1.53
Tribromomethane	1.89 ± 0.04	94.4	2.07	4.37 ± 0.24	87.3	5.41	4.64 ± 0.05	92.8	1.15	4.63 ± 0.13	92.6	2.70
1,1,2,2-Tetrachloroethane	1.71 ± 0.04	85.5	2.34	5.01 ± 0.17	100.2	3.33	4.82 ± 0.11	96.4	2.26	4.78 ± 0.08	95.6	1.65
Isopropylbenzene	1.96 ± 0.14	97.9	6.88	4.72 ± 0.11	94.4	2.32	4.77 ± 0.15	95.4	3.23	4.83 ± 0.13	96.6	2.59
N-Propylbenzene	2.01 ± 0.14	100.3	7.12	4.76 ± 0.12	95.2	2.41	4.72 ± 0.11	94.3	2.31	4.78 ± 0.11	95.7	2.37
1,3,5-Trimethylbenzene	1.99 ± 0.11	99.6	5.55	0.74 ± 0.11	94.7	2.28	5.20 ± 0.23	104.1	4.46	4.99 ± 0.18	99.8	3.57
1,2,4-Trimethylbenzene	2.04 ± 0.09	102.1	4.29	4.79 ± 0.21	95.8	4.39	5.17 ± 0.18	103.5	3.49	5.00 ± 0.17	100.1	3.40
1,3-Dichlorobenzene	2.02 ± 0.07	100.8	3.52	4.98 ± 0.10	99.6	2.05	4.83 ± 0.11	96.6	2.31	4.72 ± 0.16	94.4	3.44
1,4-Dichlorobenzene	2.02 ± 0.06	100.9	2.83	4.98 ± 0.16	99.7	3.15	4.79 ± 0.10	95.7	2.03	4.69 ± 0.16	93.9	3.41
1,2-Dichlorobenzene	1.99 ± 0.03	99.5	1.72	5.00 ± 0.14	100.0	2.86	4.70 ± 0.07	94.0	1.50	4.65 ± 0.14	93.1	2.93
1,3,5-Trichlorobenzene	2.05 ± 0.07	102.3	3.21	4.77 ± 0.17	95.4	3.63	4.77 ± 0.26	95.3	5.56	4.83 ± 0.36	96.6	7.52
1,2,4-Trichlorobenzene	2.02 ± 0.04	101.0	2.06	4.80 ± 0.26	96.0	5.38	4.63 ± 0.13	92.5	2.83	4.70 ± 0.12	94.0	2.64
Naphthalene	1.91 ±0.05	95.7	2.41	4.92 ± 0.36	98.5	7.40	4.73 ± 0.07	94.7	1.40	4.73 ± 0.12	94.7	2.46
Hexachloro-1,3-butadiene	2.01 ± 0.20	100.6	6.05	4.40 ± 0.22	88.1	4.91	4.92 ± 0.29	98.4	5.95	4.84 ± 0.13	96.8	2.69

Table 3 Intra and inter-day precision results of VOCs *(Continued)*

Compound	Intra-day (repeatability)						Inter-day (reproducibility)					
	2 µg/L (n = 6)			5 µg/L (n = 6)			Day 1 (5 µg/L (n = 6))			Day 2 (5 µg/L (n = 6))		
	Measured (µg/L)	Recovery (%)	RSD (%)	Measured (µg/L)	Recovery (%)	RSD (%)	Measured (µg/L)	Recovery (%)	RSD (%)	Measured (µg/L)	Recovery (%)	RSD (%)
1,2,3-Trichlorobenzene	2.07 ± 0.02	103.6	1.04	5.22 ± 0.36	104.4	6.93	4.89 ± 0.18	97.8	3.74	4.96 ± 0.09	99.3	1.77

[a]Measurement of p&m-xylene was performed for 4 µg/L and 10 µg/L VOC solutions
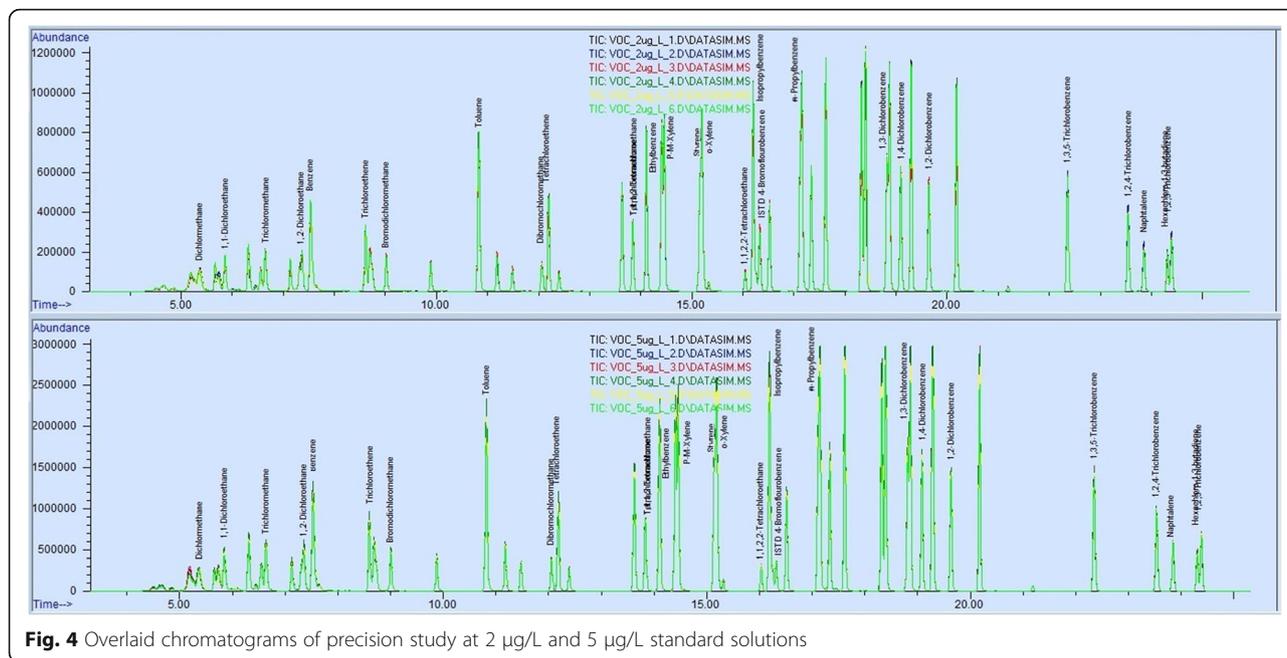
Fig. 4 Overlaid chromatograms of precision study at 2 μg/L and 5 μg/L standard solutions

results obtained in Table 4 were satisfactory and comparable to those obtained by other laboratories participating in the round. The results indicate that the method is not affected by a significant systematic error that may cause incorrect results, except for random error. In conclusion, both results of CRM and proficiency test indicate that this method is rather good and sufficient capability for the rapid and sensitive determination of possible thirty VOCs in drinking waters.

Measurement uncertainty

The study about method validation has an important role in explaining the reliability and accuracy of method results. However, this is not enough by oneself to commentate and compare the results accommodately. It should be stated the measurement uncertainty as well as the method validation (Rozet et al. 2011). The uncertainty of VOCs in drinking water samples was decided by using PT-GC/MS. The uncertainties in the study were used as parameters to identify the standard combined uncertainty, expanded uncertainty, and relative uncertainty based on the related guidelines (EURACHEM/CITAC 2012; EURACHEM/CITAC 2015). Therefore, the following individual source parameters were taken into account for the calculation of the uncertainties of VOCs in this study: (a) standard preparation (Std), (b) sample preparation (Sample), (c) calibration curve (Cal), and (d) repeatability (Rep).

- In compliance with these individual uncertainty sources, the standard combined uncertainty of the

VOCs is calculated with the following equation (Eq. (5)):

$$\frac{u_{\text{combined}}}{Conc} = \sqrt{\left(\frac{\text{u}(Std)}{Std}\right)^2 + \left(\frac{\text{u}(\text{Sample})}{\text{Sample}}\right)^2 + \left(\frac{\text{u}(Cal)}{Cal}\right)^2 + \left(\frac{\text{u}(Rep)}{Rep}\right)^2}$$

(5)

- Calculation of the uncertainty derived from calibration curve, u(Cal) (Eq. (6)):

$$u(c_o) = \frac{S}{B_1} + \sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(c_o - c_{\text{average}})^2}{S_{xx}}} \ S_{xx}$$

$$= \sum_{i=1}^{n} (c_i - c_{\text{average}})^2$$

(6)

where S is the standard deviation, B_1 is the slope, p is the number of measurements to determine c_o, n is the number of measurements for the calibration, c_o is the analyte concentration in drinking water sample, c_{average} is the mean value of the different calibration standards (n number of measurements), i is the index for the number of measurements to obtain the calibration curve, and c_i is the individual calibration standard value obtained from the calibration equation.

- Calculation of the uncertainty derived from repeatability, u(Rep):

Table 4 CRM and inter-laboratory test results for VOCs

Compounds	CRM				Proficiency test			
	Certified value (µg/L)	Measured value (µg/L)	Recovery (%)	RSD (%)	Reported value (µg/L)	Assigned value (µg/L)	SDPA (µg/L)	z-score
Dichloromethane	54.6	52.44 ± 1.14	96.0	1.82	< 6.00	< 6.00	–	–
1,1-Dichloroethane	42.4	43.18 ± 1.84	101.8	3.22	33.34	38.3	8.0	−0.618
Trichloromethane	83.1	90.87 ± 1.44	109.43	1.47	63.90	55.8	4.9	1.640
1,2-Dichloroethane	48.0	47.77 ± 0.33	99.5	0.69	115.3	118.0	3.9	−0.735
Benzene	17.0	18.68 ± 0.33	109.9	1.79	83.41	74.6	12.1	0.729
Trichloroethene	75.2	80.59 ± 1.71	107.2	2.00	90.12	81.2	11.2	0.796
Bromodichloromethane	41.2	40.47 ± 0.39	98.2	0.95	61.84	65.2	5.5	−0.611
Toluene	11.0	11.04 ± 0.19	100.4	1.72	16.98	18.4	7.3	−0.190
Dibromochloromethane	< 6.00	0.53 ± 0.01	–	0.83	72.05	73.9	7.7	−0.237
Tetrachloroethene	31.3	33.92 ± 0.02	108.4	2.45	< 4.30	< 4.30	–	–
Tetrachloromethane	30.4	29.77 ± 0.42	97.9	0.71	82.72	104.0	28.1	−0.743
1,1,1,2-Tetrachloroethane	59.7	60.97 ± 0.42	102.1	0.68	139.8	130.5	18.3	0.509
Ethylbenzene	19.4	19.98 ± 0.31	103.0	1.56	< 7.00	< 7.00	–	–
P&M-Xylene	57.3	57.31 ± 0.83	100.0	1.45	62.22	54.7	9.3	0.808
Styrene	40.8	35.85 ± 0.32	87.9	0.88	< 13.00	< 13.00	–	–
O-Xylene	21.0	20.50 ± 0.19	97.6	0.94	82.81	74.1	11.7	0.745
Tribromomethane	85.6	75.26 ± 0.76	87.9	1.01	55.29	57.3	4.5	−0.452
1,1,2,2-Tetrachloroethane	63.9	55.65 ± 0.76	87.1	1.37	62.95	65.9	13.2	−0.225
Isopropylbenzene	62.7	60.34 ± 0.70	96.2	1.00	< 5.00	< 5.00	–	–
N-Propylbenzene	9.19	9.10 ± 0.16	99.0	1.73	< 5.00	< 5.00	–	–
1,3,5-Trimethylbenzene	37.5	38.54 ± 0.56	102.8	1.46	95.76	69.1	18.6	1.430
1,2,4-Trimethylbenzene	23.3	20.09 ± 0.27	86.2	1.33	76.36	64.0	15.7	0.786
1,3-Dichlorobenzene	50.4	45.26 ± 0.42	89.8	0.93	21.68	20.9	6.3	0.123
1,4-Dichlorobenzene	32.4	28.54 ± 0.30	88.1	1.04	93.97	79.0	15.2	0.987
1,2-Dichlorobenzene	< 7.00	0.08 ± 0.01	–	8.07	104,0	91.3	15.4	0.825
1,2,4-Trichlorobenzene	49.4	39.67 ± 1.50	80.3	3.77	53.67	45.4	7.9	1.040
Naphthalene	< 6.30	0.25 ± 0.02	–	9.75	66.51	62.8	12.3	0.298
Hexachloro-1,3-butadiene	< 4.30	0.06 ± 0.01	–	5.03	50.74	46.7	15.8	0.258
1,2,3-Trichlorobenzene	< 5.00	0.33 ± 0.02	–	8.04	< 5.00	< 5.00	–	–

SDPA: Standard Deviation for Proficiency Assessment

The repeatability study was explained by the standard deviation of the results of eight consecutive measurements for each VOCs on the same day. Uncertainty from reproducibility was estimated in accordance with Aslan-Sungur et al. (2014) using the following equation (Eq. (7)):

$$u(Rep) = \frac{RSD}{\sqrt{n}} \qquad (7)$$

where RSD is the relative standard deviation and n is the number of measurement (in this case, $n = 8$).

- Calculation of the uncertainty derived from standard preparation, u(Std):

Standard preparation from stock VOC solution (200 mg/L) for the calibration curve is one of fundamental source to the uncertainty budget. The preparation of standards was done by using pipette (pip) (100 μL and 1000 μL) and volumetric flask (flask) (50 mL). Thus, the uncertainty calculation of standard preparation (Eq. (8)) includes the sum of the uncertainties of stock solution and glassware used.

$$\frac{u_{(Std)}}{C_{(Std)}} = \sqrt{\left(\frac{u(pip)}{V_{(pip)}}\right)^2 + \left(\frac{u(\text{stock})}{V_{(\text{stock})}}\right)^2 + \left(\frac{u(\text{flask})}{V_{(\text{flask})}}\right)^2} \tag{8}$$

where u(pip) is the pipette uncertainty and u(stock) is the uncertainty of the stock VOC solution. u(pip) (Eq. (9)) is calculated from the square root of the sum of the squares of both the uncertainty of calibration of the pipette [u(pipcal)] and the uncertainty of temperature effect [u(temp)]. The calculation of u(flask) (Eq. (10)), which is defined as the preparation of the standard solution by using a flask, is carried out the combination of the uncertainty of calibration of the flask [u(flaskcal)] and the uncertainty of temperature effect [u(temp)].

$$u_{(pip)} = \sqrt{(\text{u(pipcal)})^2 + (\text{u(temp)})^2} \tag{9}$$

$$u_{(\text{flask})} = \sqrt{(\text{u(flaskcal)})^2 + (\text{u(temp)})^2} \tag{10}$$

Temperature effect means that the temperature variation in the laboratory was commonly accepted as ± 3 °C in (EURACHEM/CITAC 2012).

$$u(\text{temp}) = \frac{3 \, x \, V \, x \, Q}{1.73} \tag{11}$$

where u(temp) is the standard uncertainty of temperature effect, V is the measured volume of equipment such as 1000 μL for pipette, and Q is the volume expansion coefficient of the methanol (Q_{methanol}: 1.49 × 10^{-3} °C^{-1}).

- Calculation of the uncertainty derived from sample preparation, u(Sample):

Fifty-milliliter flask was used to take the sample volume and this method includes solventless sample preparation technical procedure. For this reason, the flask uncertainty (u(flask)) in (Eq. (10)) is the source of u(Sample).

Table 5 shows the overview of the contributions of the individual uncertainty sources to the measurement of investigated VOCs at 5 μg/L. The calculation of the combined and expanded uncertainties (μg/L) (based on a 95% confidence level using a coverage factor (k) of 2) of VOCs was performed for nine standards from 0.15 to 40 μg/L used in calibration. The calculated percentage of relative uncertainties for each analyte changed from 2.99 to 10.10% and it is clear that among the four sources of uncertainty, the major contributions to the uncertainty budget consist of the calibration curve and repeatability. The contribution (%) of the standard preparation to the to the measurement uncertainty budget changed from 0.57 and 1.69%, and the contribution (%) of the sample preparation to the measurement uncertainty budget ranged from 3.38 and 10.03%. Their results indicate the contributions of standard preparation and sample preparation on the uncertainty budget are almost negligible to the combined standard uncertainties.

Application to real samples

The proposed analytical method in this study was used to monitor the level of VOC residues in sixteen different drinking water brands obtained from the supermarket. More than one hundred sixty drinking water samples were analyzed with the related analytical method. In Turkey, the presence of VOCs in drinking water has been determined mostly on the basis of the thresholds set out in the European Union's Drinking Water Directive (98/83/EC), the relevant international (e.g., WHO) or national standards. Table 6 shows the limit values of relevant national and international regulations for VOCs and their observed concentration ranges in the drinking water samples. Prior to analysis of real samples, the control of retention times, molecular and fragment ions of all analytes were performed by measuring a known standard of concentration. Furthermore, the retention times, target, and fragment ions of the compounds detected as positive in the chromatograms of these samples were checked by comparing the chromatographic peaks of the relative standards. The examination of total ion chromatograms of standard and actual samples was also done in detail. There were no interfering compounds that would cause false positive results in the chromatogram. In this study, dichloromethane, trichloromethane, 1,2-dichloroethane, benzene, toluene, tetrachloroethene, tetrachloromethane, ethylbenzene, tribromomethane, 1,1,2,2-tetrachloroethane, naphthalene, and hexachloro-1,3-butadiene were detected at low concentrations in the polyethylene bottled waters. The concentrations of these compounds had reported

Table 5 Measurement uncertainty study of investigated VOCs at 5 μg/L

Compounds	Measurement (μg/L)	Standard combined uncertainty (μg/L)	Expanded uncertainty (μg/L)a	Relative uncertainty (%)	Contributions (%) of the individual uncertainty sources			
					Standard preparation	Sample preparation	Calibration curve	Repeatability
Dichloromethane	4.7	0.14	0.29	5.77	0.87	5.16	58.71	35.26
1,1-Dichloroethane	4.6	0.21	0.41	8.30	0.65	3.85	68.27	27.43
Trichloromethane	4.7	0.18	0.35	7.04	0.86	5.11	81.79	12.25
1,2-Dichloroethane	4.7	0.16	0.33	6.57	0.87	5.17	75.94	18.02
Benzene	4.6	0.20	0.40	8.03	0.76	4.53	83.00	11.70
Trichloroethene	4.5	0.23	0.47	9.30	0.65	3.88	82.00	13.46
Bromodichloromethane	4.6	0.19	0.38	7.57	0.79	4.72	81.24	13.24
Toluene	4.7	0.18	0.35	7.08	0.84	4.96	79.58	14.62
Dibromochloromethane	4.6	0.21	0.42	8.42	0.67	3.96	73.79	21.58
Tetrachloroethene	4.5	0.25	0.51	10.10	0.57	3.38	75.96	20.09
Tetrachloromethane	4.6	0.18	0.37	7.31	0.83	4.91	81.69	12.57
1,1,1,2-Tetrachloroethane	4.7	0.18	0.35	7.06	0.84	5.01	80.21	13.93
Ethylbenzene	4.6	0.18	0.36	7.18	0.82	4.90	79.59	14.69
P&M-Xylene	9.3	0.35	0.70	6.97	0.84	4.96	77.91	16.29
Styrene	4.6	0.20	0.41	8.12	0.72	4.28	78.31	16.69
O-Xylene	4.7	0.14	0.27	5.43	1.04	6.21	75.45	17.30
Tribromomethane	4.6	0.19	0.37	7.45	0.70	4.16	64.14	31.00
1,1,2,2-Tetrachloroethane	4.6	0.18	0.36	7.18	0.78	4.62	73.12	21.49
Isopropylbenzene	4.6	0.18	0.37	7.30	0.78	4.61	74.87	19.75
N-Propylbenzene	4.6	0.18	0.36	7.30	0.77	4.59	74.29	20.35
1,3,5-Trimethylbenzene	4.7	0.15	0.31	6.18	0.90	5.32	72.60	21.18
1,2,4-Trimethylbenzene	4.8	0.12	0.23	4.65	1.13	6.71	67.23	24.93
1,3-Dichlorobenzene	4.7	0.14	0.29	5.75	0.98	5.83	74.95	18.24
1,4-Dichlorobenzene	4.7	0.13	0.27	5.32	1.03	6.09	71.30	21.58
1,2-Dichlorobenzene	4.8	0.13	0.25	5.10	1.04	6.19	68.17	24.60
1,3,5-Trichlorobenzene	4.7	0.13	0.27	5.39	0.96	5.68	63.80	29.57
1,2,4-Trichlorobenzene	4.8	0.09	0.17	3.49	1.36	8.07	50.47	40.10
Naphthalene	4.8	0.08	0.16	3.22	1.48	8.78	53.19	36.55
Hexachloro-1,3-butadiene	4.6	0.19	0.39	7.75	0.74	4.38	75.72	19.16
1,2,3-Trichlorobenzene	4.9	0.07	0.15	2.99	1.69	10.03	63.65	24.64

a*k* = 2, 95% confidence level

similar results in the literature (Leivadara et al. 2008; Al-Mudhaf et al. 2009; Ikem 2010). These substances were positively detected in forty-eight drinking water samples within the ranges summarized in Table 6 and there were no individual VOC parameters exceeding national and international limits (EU 1998; RCWHC 2005; WHO 1993; WHO 2001). Six-point calibration curves by fitting its area ratio were applied for the quantification of analytes.

Conclusion

The verification study of proposed method has been performed for the simultaneous analysis of the presence of possible thirty VOCs in drinking waters by direct injection to PT-GC/MS in compliance with national and international legislations such as European Union's Drinking Water Directive (98/83/EC) regarding the quality of polyethylene bottled waters determined to human consumption. This method includes solventless sample preparation technical procedure, which is called PT

Table 6 Limit values of national and international regulations for VOCs and their observed concentration ranges in the drinking water samples (EU 1998; RCWHC 2005; WHO 1993; WHO 2001)

Compounds (µg/L)	Turkey	EPA	EU	WHO	Observed concentration ranges
Dichloromethane	–	5	–	–	0.13–0.51
1,1-Dichloroethane	–	7	–	–	< 0.10
Trichloromethane	–	–	–	–	0.10–0.30
1,2-Dichloroethane	3	5	3	30	0.16–0.39
Benzene	1	5	1	10	0.10–0.16
Trichloroethene	10	5	10	70	< 0.10
Bromodichloromethane	–	–	–	–	< 0.10
Toluene	–	1000	–	700	0.14–0.58
Dibromochloromethane	–	–	–	–	< 0.10
Tetrachloroethene	10	5	10	40	0.39–0.41
Tetrachloromethane	–	5	–	2	0.10–0.13
1,1,1,2-Tetrachloroethane	–	–	–	–	< 0.10
Ethylbenzene	–	700	–	300	0.15-0.23
P&M-Xylene	–	–	–	–	< 0.10
Styrene	–	100	–	20	< 0.10
O-Xylene	–	–	–	–	< 0.10
Tribromomethane	–	–	–	–	0.15–0.46
1,1,2,2-Tetrachloroethane	–	–	–	–	0.11–0.23
Isopropylbenzene	–	–	–	–	< 0.10
N-Propylbenzene	–	–	–	–	< 0.10
1,3,5-Trimethylbenzene	–	–	–	–	< 0.10
1,2,4-Trimethylbenzene	–	–	–	–	< 0.10
1,3-Dichlorobenzene	–	–	–	–	< 0.10
1,4-Dichlorobenzene	–	–	–	300	< 0.10
1,2-Dichlorobenzene	-	75	–	1000	< 0.10
1,3,5-Trichlorobenzene	-	600	–	–	< 0.10
1,2,4-Trichlorobenzene	-	-	–	–	< 0.10
Naphthalene	-	-	–	–	0.13–0.16
Hexachloro-1,3-butadiene	-	-	–	0.6	0.10–0.17
1,2,3-Trichlorobenzene	-	70	–	–	< 0.10
Total Xylenes	-	10000	–	500	< 5
Total Trihalomethanes	100	–	100	–	< 5
Total Trichlorobenzenes	–	–	–	20	< 5

system. It has been validated in pursuant to ISO/IEC 17025:2017 requirements, following the AOAC and EURACHEM/CITAC validation guidelines with the assessment of selectivity, linearity, LOD and LOQ, accuracy (recovery), precision, trueness, and measurement uncertainty studies. In linearity of calibration curves, the values of correlation coefficients for the matrix-matched calibration curves were higher than 0.998 for all analytes in this study. The analytical response linearity in the working concentration range can be assessed as a great in pursuance of correlation coefficients. The dynamic linear range was determined from 0.15 to 20 µg/L for the majority of the studied VOCs except for dichloromethane, toluene, and p&m-xylene. The LOQ values were found to be in the range of 0.011 µg/L and 0.040 µg/L and the ranges of LOQ for VOCs were obtained from 0.035 to 0.133 µg/L, respectively. These results indicate high sensitivity of the method. This method reveals quite sufficient recovery (82.6% to 103.1%) for accuracy; acceptable precision (intra-day recovery: 81.5–104.4%, RSD: 1.04–9.81%; inter-day recovery: 92.6–104.1%, RSD: 1.15–7.52%). All the recovery and RSD

values obtained below 10% can be interpreted agreeable with respect to related validation guidelines. The trueness of method was evaluated with CRM and through participation in proficiency testing analyses. At the end of analysis of CRM, the recovery percentages of all analytes varied from 80.3 and 109.9% and the RSD (%) values for each analyte obtained below 10%. The results are acceptable in comparison to certified value. Moreover, there were no obtained questionable or unsatisfactory z score results in the proficiency test. In the measurement uncertainty, the calculated percentage of relative uncertainties for each analyte was changed from 2.99 to 10.10% and the calibration curve and repeatability possess powerful impacts on the combined uncertainty. On account of the high sensitivity and good accuracy obtained with the combination of PT and single quadrupole MS, developed and validated screening method were effectively proven to work and allows the analysis of thirty VOCs at low concentrations by applying drinking water samples.

Abbreviations
ASTM: American Society for Testing and Materials; COPR: Control of Pesticides Regulation; CRM: Certified Reference Material; DAR: Deutscher Akkreditierung Rat; EU: European Union; FEPA: Food and Environmental Protection Act; GC-MS: Gas Chromatography-Mass Spectrometry; IS: Internal Standard; ISO: International Organization for Standardization; LOD: Limit of Detection; LOQ: Limit of Quantification; PCR: Prevention and Control Regulation; PT: Purge & Trap; RSD: Relative Standard Deviation; TUBITAK MAM: The Scientific and Technological Research Council of TURKEY Marmara Research Center; TURKAK: Turkish Accreditation Agency; UK: United Kingdom; VOCs: Volatile Organic Compounds; VVOC: Very Volatile Organic Compounds; WHO: World Health Organization

Authors' contributions
OC conceived of the study and carried out the design of experiment. BG carried out the sample preparation and analysis, assessment of data, and helped to draft the manuscript. The author(s) read and approved the final manuscript.
Ethics approval and consent to participate
Not applicable.

Availability of data and materials
Research data have been provided in the manuscript.

Consent for publication
Not applicable.

Competing interests
The authors declare that they have no competing interests.

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