Optimization of Static Head-Space Gas Chromatography - Mass Spectrometry-Conditions for the Determination of Benzene, Toluene, Ethyl benzene, Xylene, and Styrene in Model Solutions

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Abstract

A method was developed and validated for the analysis of benzene, toluene, ethylbenzene, xylene (BTEX), and styrene in sea water samples using gas chromatography-mass spectrometry (GC-MS) with static head-space extraction. To carefully characterize the performance of this method, several factors affecting the parameters were studied in detail, such as the heating procedure, loop filling time, equilibrium temperature, the sample dilution ratio, equilibrium, and injection times. The optimized conditions are as follows: 1)the heating procedure, 50°C for 4 min, then increased to 170°C at 15°C min^{-1}, 2) equilibrium temperature, 60°C, 3) equilibrium time, 5 min, and 4) injection time 0.5 min. Under the optimized conditions, the linear equations were obtained in the concentration range of 10 - 50 μg L^{-1} with good correlation coefficient values. The limits of detection were 1.8 - 3.3 μg L^{-1}. The recoveries at the spiked level of 20 μg L^{-1} BTEX and styrene ranged from 97% - 103% with the relative standard deviations were (RSD, n=3) 1.0% - 7.6%. The method was used for seawater samples from the Marmara Mudanya region.

Keywords: BTEX, Gas chromatography–mass spectrometry, Sea water, Static Head-space, and Styrene.

Model Çözeltilerde Benzen, Toluen, Etil Benzen, Ksilen ve Stirenin Tayini için Statik Headspace-Gaz Kromatografisi-Kütle Spektrometresi Şartlarının Optimizasyonu
Özet

Deniz suyundaki benzen, toluen, etilbenzen, ksilen ve stiren bileşenlerinin tayininde gaz kromatografisi metodu kullanılmaktadır. Bunun için örnekler statik buhar faz ekstraksiyon yöntemiyle gaz faza alınıp gaz kromatografisi kütle spektrometresine enjekte edilmektedir. Analiz sonuçlarına etki edebilecek parametrelerden en önemlileri araştırılarak, gerçek deniz suyu örneğinin film kompozisyonu en önemli faktör olarak saptanmıştır. Cihazda kullanılan fırın programı; 50°C, 4 dk boyunca, 15°C dk^{-1} artış hızı ile 170°C' ye ısınma şeklindedir. Enjektör sıcaklığı 280°C' dir. Optimize edilen şartlarda, kullanılan analitik bölge aralığında (10-50 μg L^{-1}), yüksek korelasyon katsayıları elde edilmiştir. Gözlenebilme sınırları 1,8-3,3 μg L^{-1} aralığındadır. Geri kazanım verimleri, 20 μg L^{-1} katılımlar için %97'nin üzerinden bulunurken, bağıl standart sapmalar ise %1 ile %8 arasında değişmektedir. Geliştirilen yöntem Marmara Denizi Mudanya kıyılarından alınan deniz suyu örneklerine uygulanmıştır.

Anahtar Kelimeler: BTEX, Deniz Suyu, Gaz Kromatografisi - Kütle Spektrometresi, Statik Buhar faz ekstraksiyonu, Stiren

INTRODUCTION

Volatile organic compounds (VOCs), such as benzene, toluene, ethyl benzene, m-xylene (BTEX), and styrene, are a family of important environmental pollutants which have gained greater attention in sea water monitoring. Compounds of BTEX and styrene enter the environment from different sources such as the combustion of wood products and fuels, industrial paints, adhesives, degreasing agents, protective coatings, ion-exchange resins, and aerosols (Menendez et al. 2000, Silve et al. 2000, Dongqiang et al. 2006, Toledo et al. 2010, Hashemi et al. 2012). The majority of BTEX and styrene released into the environment enter the atmosphere directly. BTEX may be introduced into water or seawater by industrial effluents and atmospheric pollution, but releases of BTEX into water are mainly related to spills of petrol and petroleum products or a proximity to natural deposits of petroleum and natural gas. Toxicity testing for

BTEX compounds has also been conducted on aquatic organisms. Typically water concentrations in excess of 1 mg L⁻¹ are required to produce acute toxic effects in organisms such as algae, dauphins, and fish (Leusch et al. 2010). The maximum contamination levels (MCLs) according to the U.S. Environment Protection Agency (EPA) for benzene, toluene, ethylbenzene, and xylene are 0.005, 1, 0.7, and 10 mg L⁻¹, respectively, and concentrations above the MCLs in air and water seriously affect human health (Anonymous 2004). Due to low background concentrations of these chemicals in water, rapid volatilization and degradation processes and their low to moderate toxicity, the overall risk to the aquatic environment is therefore considered low (Anonymous 1996, Anonymous 1997). BTEX are hazardous carcinogenic and neurotoxic compounds, and are classified as priority pollutants by the US EPA (Wang et al. 1995).

According to 76/160/ EEC, the quality requirements of bathing water were outlined with microbiological and physicochemical parameters, in which other substances may be included in the assessment of pollutant level to be checked by competent authorities when an inspection in the bathing area shows that the substance may be present or that the quality of the water has deteriorated (Anonymous 1975).

There is, therefore, a vital need to develop simple and cheap analytical methods with low detection limits for the quantification of BTEX. The aim of the present work is to investigate the applicability of the static head-space for the extraction and determination of BTEX and styrene in seawater samples by gas chromatography-mass spectrometry (GC-MS). All the experimental parameters affecting the extraction procedure were intensively investigated and analytical characteristics of the method were also evaluated. Sea water samples were analyzed to demonstrate the applicability of the proposed method.

MATERIAL AND METHODS

Apparatus

The Agilent G1888 Network Head-space sampler was used to directly introduce samples automatically into the Agilent 7890A GC gas chromatography-5975 C inert XL MSD model mass spectrometer (GC–MS) equipped with a 7683 B series auto sampler injection system (Agilent Technologies, Palo Alto, CA). Analysis was carried out using an Agilent 7890A GC gas chromatograph equipped with a flow modulator (Agilent G3180 CFT Modulator). The effluent from the column is split one part to the flame ionization detector (FID) and the other to the mass spectrometry (MSD) detector (5975 C inert XL MSD, Agilent Technologies, Palo Alto, CA). A deactivated splitter (Agilent Technologies) was used. Two parallel deactivated fused silica capillaries were connected to the splitter with the approximate split ratio of 2:1 (MS: FID). Separation was performed on a HP-5 ms fused-silica capillary column (30 m × 0.25 id., with a 0.25 mm film thickness). The carrier gas was helium (He) with a constant flow rate of 1 mL min⁻¹. The GC oven temperature was initially set at 50°C for 4 min, and then was increased to 170°C at a heating rate of 15°C min⁻¹ and held for 5 min. The quadrupole MSD transfer line temperature was set at 280°C. Electron ionization mass spectra in the SIM mode was recorded at 70 eV electron energy. The working conditions of the head-space are given in Table 1. All data was recorded using the MS ChemStation. The samples were analyzed in triplicate and blank runs were done before and after each analysis. Retention times and the identification and quantification of ions selected for the target compounds are shown in Table 2. The selective ion chromatogram of 0.1 mg L⁻¹ standard is given in Fig. 1.

Reagents

All solvents used were of analytical reagent grade. A multi-compound standard VOC Mix 5 (Dr. Ehrenstorfer GmbH, Augsburg, Germany) was used for the GC–MS calibration. Stock solutions were stored at 4°C in a refrigerator. Fresh solutions were prepared daily by diluting the different amounts of the standard stock solutions in double distilled water to the required concentrations. The Distilled Water used was ultrapure grade (18.2 megaohm, mX cm⁻¹ Zeener Power Human Corp, Japan)

Sampling

The sea water samples were collected from the Marmara Sea in the Güzelyalı, Mudanya region . Five milliliters of sample was immediately placed in the head-space vials and tightly closed.

RESULTS AND DISCUSSION

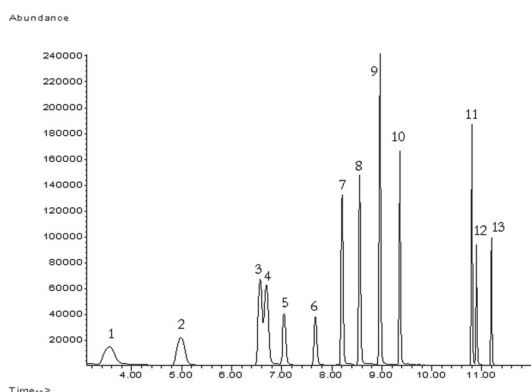Although there is a large amount of work on the metal analysis of sea waters in Turkey, there are no

Fig 1. GC–MS selective ion chromatogram of 0.1 mg L-1 standards (Peaks identification: (1) benzene, (2) toluene, (3) ethylbenzene, (4) m- xylene, (5) styrene, (6) bromobenzene, (7) 1,3,5-trimethylbenzene, (8) 1, 2, 4-Trimethylbenzene, (9) p-Isopropyl toluene, (10) n-butyl benzene, (11) 1,2,3-trichlorobenzene, (12) naphthalene, and (13) 1,2,4-trichlorobenzene).

Table 1. The working conditions of the head-space unit.

Parameters	
Oven temperature	60 ºC
Loop temperature	110 ºC
Transfer line temperature	120 ºC
GC cycle time	13 min
Vial equilibrium time	5 min
Pressure time	0.15 min
Loop fill time	0.5 min
Loop equilibrium time	0.10 min
Injection time	1 min
Shake mode	high
Vial pressure	8 kPa

Table 2. Retention times and selected ions for the analysis of the target compounds.

Compound	Retention Time (t_R)	Molecular weight (g mol^{-1})	m/z	Sea water solubility (mg L^{-1}) (Neff J.M.2002)
Benzene	3.526	78	78[a], 52[a], 41	1398
Toluene	4.964	92	91[a], 65[a], 51	389
Ethyl benzene	6.560	106	106[a], 91[a], 77, 65, 51	114
m-Xylene	6.688	106	106[a], 91[a], 77, 65, 51	108
Styrene	7.038	104	104[a], 78[a], 51	-

[a] quantification of ions selected for the target compounds

studies related to the analysis of BTEX (Ayas et al. 2009, Balkis et al. 2012, Alp et al. 2012, Ozkan et al. 2012). Due to the toxic properties of these compounds, development of specific analytical procedures for analysis of these compounds in the various matrices is of great importance. GC is the main alternative   choice for the determination of BTEX in environmental samples. Since the matrices of environmental samples are often complex, sample preparation plays an important role in the

determination of these species. For the determination of VOCs in aqueous matrices, direct injection of sample, liquid–liquid extraction (Golfinopoulos et al. 2001), static head-space techniques (Safarova et al. 2004), dynamic head-space techniques (Hashimoto et al. 2001, Wang et al. 2001, Nikolaou et al. 2002), solid-phase extractions (SPE), solid-phase micro extractions (SPME) (Llompart et al. 1998, Sarrion et al 1999, Stack et al. 2000, Yang et al. 2001, Ezquerro et al. 2003), and thermal desorption (Kilic et al. 2004) are used as sample preparation techniques. The static head-space sampling is a suitable sampling technique for determining VOCs by GC. Although the direct analysis of the samples' headspace has been traditionally employed for their determination (Perez-Pavon et al. 2004, Serrano et al. 2004), new extraction strategies including the so-called solventless sample preparation techniques are gaining importance (Wardencki et al. 2007, Lambropoulou et al. 2007), since they improve the selectivity and sensitivity of the developed methodologies. The head-space offers several advantages: it is not expensive, does not require complicated instrumentation, the use of organic solvents is not necessary and the sensitivity for BTEX and styrene is dramatically enhanced compared with direct injection technique (Voice 1994, Hewitt et al. 1998). Furthermore, head-space analysis for BTEX and other VOCs has been adopted by the US EPA in several protocols (EPA Method 524.2). However, the equipment required is not cheap and the sensitivity may not be enough for samples with very low levels of BTEX. In fact, head-space sampling is suitable for the analysis of samples with rather high contents of volatile compounds (e.g. waste waters, seawaters) (Ketola et al. 1997, Zwiener 1998). Few studies have been conducted with seawater on the analytical method improvements for BTEX and styrene analysis with head-space GC-MS.

Optimization of Static Head Space Conditions

The sensitivity of the static head-space method is limited by the concentration of the VOC in the head-space. This concentration depends on the initial concentration in the water, the phase ratio between liquid phase and gas phase, and the water/air distribution constant. The static head-space method is simple and involves the

thermodynamic equilibrium of volatile substances within the aqueous and the gas phase of the sample in a closed thermostated vial. The gas phase containing the volatile substances is injected into the GC column and analyzed (Voice et al. 1993) without the influence of the matrix. The concentration of the analyte (Cg) in the head-space depends on the partition coefficient (K) of the analyte, the initial analyte concentration (Co) and the volume ratio (β) of the gas phase to the liquid phase at equilibrium as described by equation(1):

$$C_g = \frac{C_o}{K + \beta} \qquad (1)$$

Since K is temperature dependent, the temperature of equilibration influences the head-space GC (Kolb et al. 1997).

Important parameters which may influence BTEX and styrene analysis are discussed below.

Effect of Equilibrium Time

Extraction was performed from 1 to 10 min to determine the effect of extraction time. Fig. 2 shows the relative peak area versus extraction time profiles for the analyst. It can be seen that equilibrium is attained after 5 min. After this time, the extraction efficiency did not change significantly for most of the analytes. Under these conditions, the analyte concentration equilibrium between head-space and water media is reached. However, the increase on the peak areas for these analytes after 5 min extraction can be considered as not significant, but literature results show that there is a degeneration on the method precision for longer extraction times (Eshagi et al. 2011). Therefore, the extraction time was fixed in 5 min.

Effect of Extraction Temperature

During the extraction, it was necessary for the solute to vaporize from the sample solution to the gas phase by heating the sample. On the other hand, increasing extraction temperature could increase the head-space and sample partition coefficient of the analyte. The optimal extraction temperature was investigated by exposing the sample for 5 min to temperatures ranging from 40 to 70°C, which is illustrated in Fig. 3. As shown in Fig. 3, the extracted quantity of BTEX compounds increased with temperature. In order to reduce water vapour, 60°C was preferred as the optimum extraction temperature.
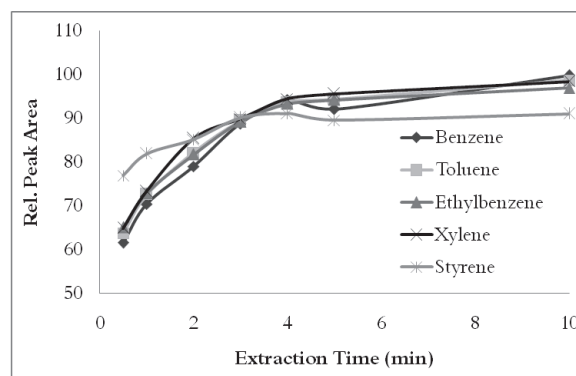

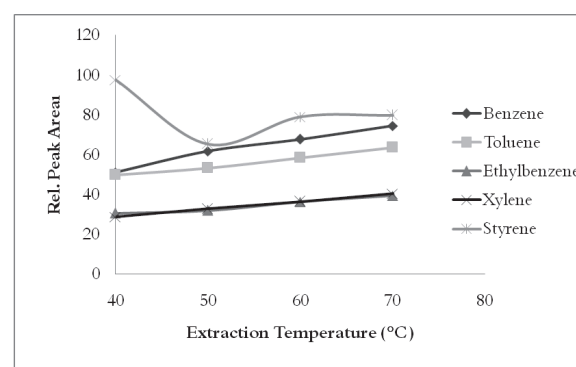**Fig 2.** Effect of the extraction time on the relative peak area.

Fig 3. Effect of the extraction temperature on the relative peak area.

Effect of Loop Filling Time

The loop fill time effect that was observed is shown in Fig. 4. Short times increase the signal for BTEX analysis because short times avoid equilibration of the loop at atmospheric pressure; as the sample inside the loop is kept at a high pressure, the analytes are more concentrated with the subsequent improvement of the sensitivity of the determinations. A loop filling time of 0.5 min was selected.

Effect of Salt Composition

Concentration of the VOC depends on solute characteristics (vapour pressure, and water solubility), temperature, pressure, pH, and salt concentration. Addition of salt to the aqueous sample is usually made to improve the extraction of several analytes because the increase in ionic strength brings a reduction on the solubility of the hydrophobic analytes in the water solution and forces more of these analytes into the head-space and the extracting phase. The salting-out effect was examined by monitoring the variation of peak areas in the presence of different sample dilution ratios.
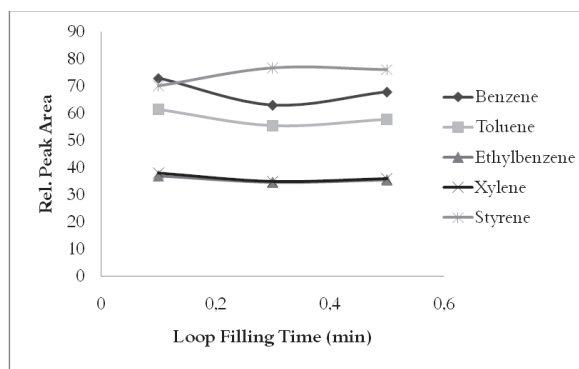
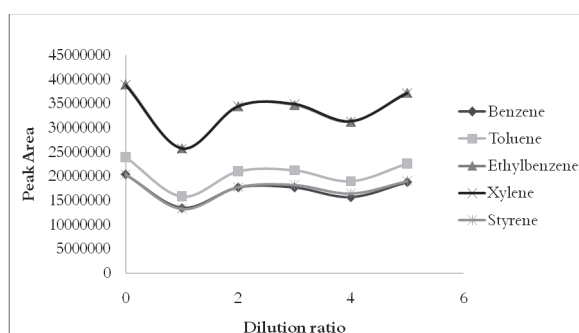**Fig 4.** Effect of the loop filling time on the relative peak area.

Fig 5. Effect of the sample dilution ratio on the peak area.

The effect of sample (matrix) dilution ratio on the peak area is shown in Fig. 5. The initial decrease of peak areas could be explained by the salting-out effect. For the secondary increase of the peak areas, it could be explained by the film effect, which promotes analytes to move to the water surface film and therefore reduced the interaction with the head-space. Extensive areas of the sea's surface have been observed to be covered with organic films or slicks from shipping and other human pollution near shore and from natural biological processes in the open sea. A scum sample formed by film collapse was collected near the costal sea water and contained about 27% organic material (Ewing 1950). Analysis of the water insoluble organic components of the film materials collected from the ocean revealed fatty esters, acids and alcohols, and hydrocarbons the relative amounts being dependant on the meteorological and oceanographic conditions prevalent at the location when the sample was taken. These films affect several of the surface properties of the sea which may result in different evaporation behaviours (Horne 1969). The vapour pressure is regulated by Raoult's Law but in some cases

Table 3. Analytical performance characteristics of head-space GC-MS for BTEX determinations in seawater samples.

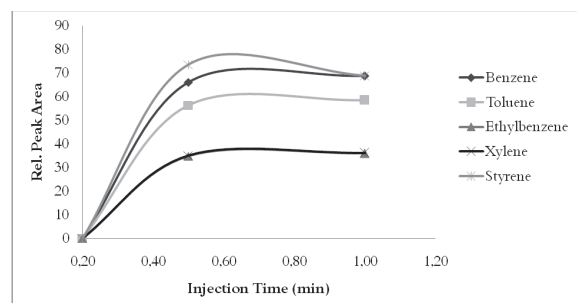| Compound	LOD ($\mu g\ L^{-1}$)	R^2	Precision (% R.S.D.)		Linear range ($\mu g\ L^{-1}$)
			Inter day	Intra day	
Benzene	2.6	0.994	2.3	5.2	10-50
Toluene	2.6	0.989	2.0	5.3	10-50
Ethylbenzene	3.2	0.993	3.7	4.8	10-50
m- Xylene	1.8	0.988	1.0	5.7	10-50
Styrene	3.3	0.999	7.6	12.6	10-50

Fig 6. Effect of the injection time on the relative peak area.

deviations have to be calculated if the vapour pressure will be greater than expected from Raoult's law, showing positive deviation and the vapour pressure curve will show a maximum at a particular composition and form a positive azeotrope. In order to reach the maximum peak area, the sea water sample was not diluted.

Effect of Injection Time

Injection was performed in a range of 0.2 to 1 min to determine the effect of injection time on the relative peak area. Fig. 6 shows the relative peak area versus injection time profiles for the analytes. After 0.3 min, the injection time did not change significantly for most of the analytes.

Analytical Figures of Merit

Quality factors, including the limit of detection (LOD), linear range, correlation coefficient (R^2), and repeatability, were investigated to evaluate the analytical performance of the proposed method under the optimal conditions. The obtained values for the described quality factors are presented in Table 3. Linearity of the calibration curve was observed in the range of 10 - 50 $\mu g\ L^{-1}$ with good R^2 values. Inter-day and intra-day precision tests (n=3) were carried out by extracting a spiked seawater sample of 20 $\mu g\ L^{-1}$. No BTEX and styrene were detected in the sea water samples within the LODs.

CONCLUSION

In this study, a standard analytical method was

validated for the analysis of BTEX and styrene in real sea water samples by means of a static head-space analysis and GC-MS. The separation was achieved by a multipurpose standard column (HP-5 ms). The method allows an easy sample preparation, a reproducible separation, and precise and accurate detection of analytes. It was observed that the key parameter for an accurate result was the sea sample which may have a different film composition. The results will also have a great importance in the studying of the air sea interface processes. In the case of sensitivity improvements most of enrichment techniques can be combined. The obtained quantification limits can be easily applied for screening BTEX and styrene in coastal and open sea environments. The method can be also applied for the microbial degradation of hydrocarbon in sea water.

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