Gas chromatographic determination of benzene, toluene, ethylbenzene and xylenes using flame ionization detector in water samples with direct aqueous injection up to 250 μl

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Abstract

A simple method of solventless extraction of volatile organic compounds (benzene, toluene, ethylbenzene and xylenes) from aqueous samples was developed. This method allows direct injection of large volume of water sample into a gas chromatograph using the sorption capacity of the sorbent Chromosorb P NAW applied directly in the injection port of gas chromatograph. The system prevent water penetration into a column, keep it adsorbed on its surface until the analytes are stripped into a column, and the residual water is purging using split flow. The limit of detection ranging from 0.6 for benzene to 1.1 $\mu g \, l^{-1}$ for o-xylene and limit of quantification ranging 2.0–3.6 $\mu g \, l^{-1}$ are lower that those reached by gas chromatography with flame ionization detection and direct aqueous injection before.
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1. Introduction

The analytical methods based on solventless sample preparation techniques for environmental samples which allow elimination of liquid solvents in the analytical procedures at low concentration levels as well as the reduction of the sample preparation time are permanently in development [1]. The method avoiding usage of sample preparation is direct aqueous injection (DAI) [2–4]. DAI presumes analysis of volatile organic compounds in water samples by direct injection of water sample into a chromatographic column. The sample pre-treatment and pre-concentration steps elimination helps to minimize the losses of volatile analytes as well as possibility of sample contamination. The major disadvantage is that water is not compatible with stationary film of capillary columns and with flame ionization detector (FID), as well [5–7].

The volatile aromatic compounds such as benzene, toluene, ethylbenzene, *ortho*-, *meta*-, *para*-xylene (BTEX) are fuel components commonly found in ground water contamination. The normalized quality limit for drinking water according EPA is for benzene 5, toluene 1000, ethylbenzene 700 and for xylenes 10000 $\mu g \, l^{-1}$, respectively [8]. The analysis of BTEX in aqueous samples is usually achieved by purge-and-trap (PTI) gas chromatography (GC) [9]. In order to determine water samples with concentration of BTEX on trace levels without any pre-treatment, it is necessary to inject large volumes of 0.1–1 ml of water sample [5], needed to be prevented from entering capillary column of gas chromatograph. The upper limit for direct aqueous injection acceptable in capillary GC is 10 μl [6].

The aim of this work was to develop a new simple method enables direct injection of large volume of water sample into a gas chromatograph. This method use the sorption capacity of the sorbent Chromosorb P NAW applied directly in the injection port of gas chromatograph to prevent water from penetrating into a column, but keep it adsorbed on its surface

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until the analytes are stripped into a column, and the residual water is purging using split flow.

The experimental parameters as injection port temperature, water sample injecting volume and concentration of analytes in relationship to stripping efficiency of analytes in time as well as linearity of calibration dependences and limits of determination and quantification were investigated.

2. Experimental

2.1. Materials

Chromosorb P NAW 60–80 mesh with a specific surface area of $5 \, m^2 \, g^{-1}$, packing density of $0.35 \, g \, ml^{-1}$ and upper temperature limit of $350 \, °C$ as packed materials were purchased from Supelco (Bellafonte, PA, USA). The liner (splitless single-taper, $900 \, \mu l$ volume) is full of sorbent up to two-third of its volume. Standards BTEX (benzene, toluene, ethylbenzene, *p*- and *o*-xylene) were from Slovak Institute of Metrology (Bratislava, Slovakia), and methanol (gradient grade) from Merck (Darmstadt, Germany).

Glass syringes for water sampling (volumes 5, 10, 25, 100, and $250 \, \mu l$) were from Hamilton (Bonaduz AG, Switzerland).

Restrictor as an uncoated deactivated silica capillary column of $0.3 \, m \times 0.1 \, mm$ from CACO (Bratislava, Slovakia) was used for investigation of the sorption–desorption process of analytes in replete GC liner, and a DB-1 $30 \, m \times 0.32 \, mm$ i.d. $\times 5 \, \mu m$ column (J&W Scientific, Blue Ravine Road, Folsom, USA) was employed for analytical separation of desorbed aromatic hydrocarbon standards.

2.2. Optimization of sorption–desorption conditions

The influence of three independent variables x_i, x_T – temperature of injection port, x_V – sampling volume and x_C – concentration of analytes, on sorption–desorption process were investigated. The optimization process was performed using the method of experiment planning according Box-Hunter [10] to reach the maximum information at minimum number of measurements. Considering listed x_i; 20 measurements were needed to perform at combination of assigned values for analyte concentration, temperature of injection port and sampling volume for each selected analyte. These experiments were performed for benzene and *o*-xylene, the least and the most sorbed analytes, respectively. From obtained chromatograms was determined the time when the 95% of the most sorbed analyte (*o*-xylene) is stripped into the column. Results were used for optimization test done by MATLAB 5.3 program using relevant coefficients (-1.68, -1, 0, 1 and 1.68) according the Box-Hunter plan instead of real values of independent variables.

2.3. Sampling

Drinking water samples ($100 \, ml$) were spiked with 1.27, 4.0, 8.0, 12.0 and $14.7 \, mg$ of benzene and *o*-xylene standard apart for investigation of desorption of analytes from sorbent placed in the liner of GC injector. Concentration of benzene and *o*-xylene in drinking water models were 12.7, 40.0, 80.0, 120 and $147 \, mg \, l^{-1}$. Sampling volumes were 15.9, 50.0, 100, 150 and $184.7 \, \mu l$ at injection port temperature 53, 60, 70, 80 and $87 \, °C$. The values of present independent variables (analyte concentration, sampling volume, injection port temperature) were assigned by the method of experiment planning according the Box-Hunter plan.

Water samples ($16 \, ml$) for optimization of GC conditions and investigation of calibration dependences were prepared by adding of $16 \, \mu l$ of methanolic solution containing $5–5000 \, mg \, l^{-1}$ of individual BTEX. Concentrations of individual BTEX in drinking water models were 5, 10, 20, 50, 100, 200, 500, 1000, 2000, and $5000 \, \mu g \, l^{-1}$. Sampling volumes were 10, 100 and $250 \, \mu l$.

Aqueous samples ($16 \, ml$) for determination of detection and quantification limits with concentration of individual BTEX 0.5, 1, 2, 3, 4, 5, 6 and $7 \, \mu g \, l^{-1}$, were prepared by adding of $1.6–22.4 \, \mu l$ of metanolic solution with concentration $5000 \, \mu g \, l^{-1}$ of individual BTEX and the sampling volume was $250 \, \mu l$.

The model water sample ($1000 \, ml$) contaminated with gasoline were prepared by adding of $1 \, \mu l$ of gasoline UNI 91 (Slovnaft, Slovakia) into river water from Danube (Bratislava. Slovakia) and the sampling volume was $250 \, \mu l$.

2.4. GC analysis

The GC measurements were performed on gas chromatograph HP 5890 Series II Hewlett-Packard (Avondale, USA) equipped with FID and a split–splitless injector. The carrier gas was helium with a pressure of $65 \, kPa$ in the injection port. The detector temperature was maintained at $250 \, °C$. Injections for investigation of sorption–desorption processes were made in the splitless mode for $6 \, min$, than split mode (flow rate $250 \, ml \, min^{-1}$) at various temperatures of injection port in the range of $53–87 \, °C$ and oven temperature $70 \, °C$ for each analyte. Injections for separation of desorbed aromatic standards from sorbent placed in the injection port liner were made in the splitless mode for $3 \, min$ (the time period of stripping and focussing of analytes from injection port into column forehead), than split mode (flow rate 250 and $400 \, ml \, min^{-1}$ at sampling volume of $250 \, \mu l$) at injection port temperature $70 \, °C$, and oven temperature $20 \, °C$ for $3 \, min$, first temperature ramp from 20 to $120 \, °C$ at $50 \, °C \, min^{-1}$ (transforming the analytes in the gas phase and removing of water from sorbent through the split vent) and the second temperature ramp from 120 to $150 \, °C$ at $1.5 \, °C \, min^{-1}$ (separation of desorbed analytes).

Data acquisition and processing were done using CSW 1.7 (APEX, Prague, Czech Republic) software.

For investigation of large volume direct aqueous injection using sorbent material placed into injection port was used a model mixture of BTEX without *m*-xylene because of its co-elution with *p*-xylene in used GC column. Results of real samples are given as sum of *m*- and *p*-xylene because these

isomers show similar recovery and response. In the case of required individual, analysis of these isomers is necessary by use other GC column which separates *m*- and *p*-xylene.

2.5. Calculation of detection and quantification limits

The detection limits (LOD) were calculated by using a signal-to-noise ratio of 3:1, the quantitation limits (LOQ) by using a signal-to-noise ratio of 10:1.

3. Results and discussion

3.1. Analytical system for large volume direct aqueous injection

A new analytical system with adsorbent inside of the liner of GC injection port was developed for the pre-concentration of trace volatile organic compounds (BTEX) from aqueous samples at direct large volume aqueous injection. The liner full of sorbent serves as a sponge restraining water while analytes are stripped into a capillary column. The large volume (up to 250 μl) of water is injected into injection port of gas chromatograph at splitless mode, low injection port temperature (70 °C) and low oven temperature (20 °C) when the analytes are striping and focusing into the column while the water remains in the injection port (Fig. 1A). To reach better focusing of analytes on column forehead the column with 5 μm thickness of stationary phase was used. After the striping period (3 min) the split vent is opened together with starting of oven temperature program and the water is removed from GC system whereas the analytes starting to separate (Fig 1B). Desorbed analytes are separated by capillary gas chromatography and detected by FID.
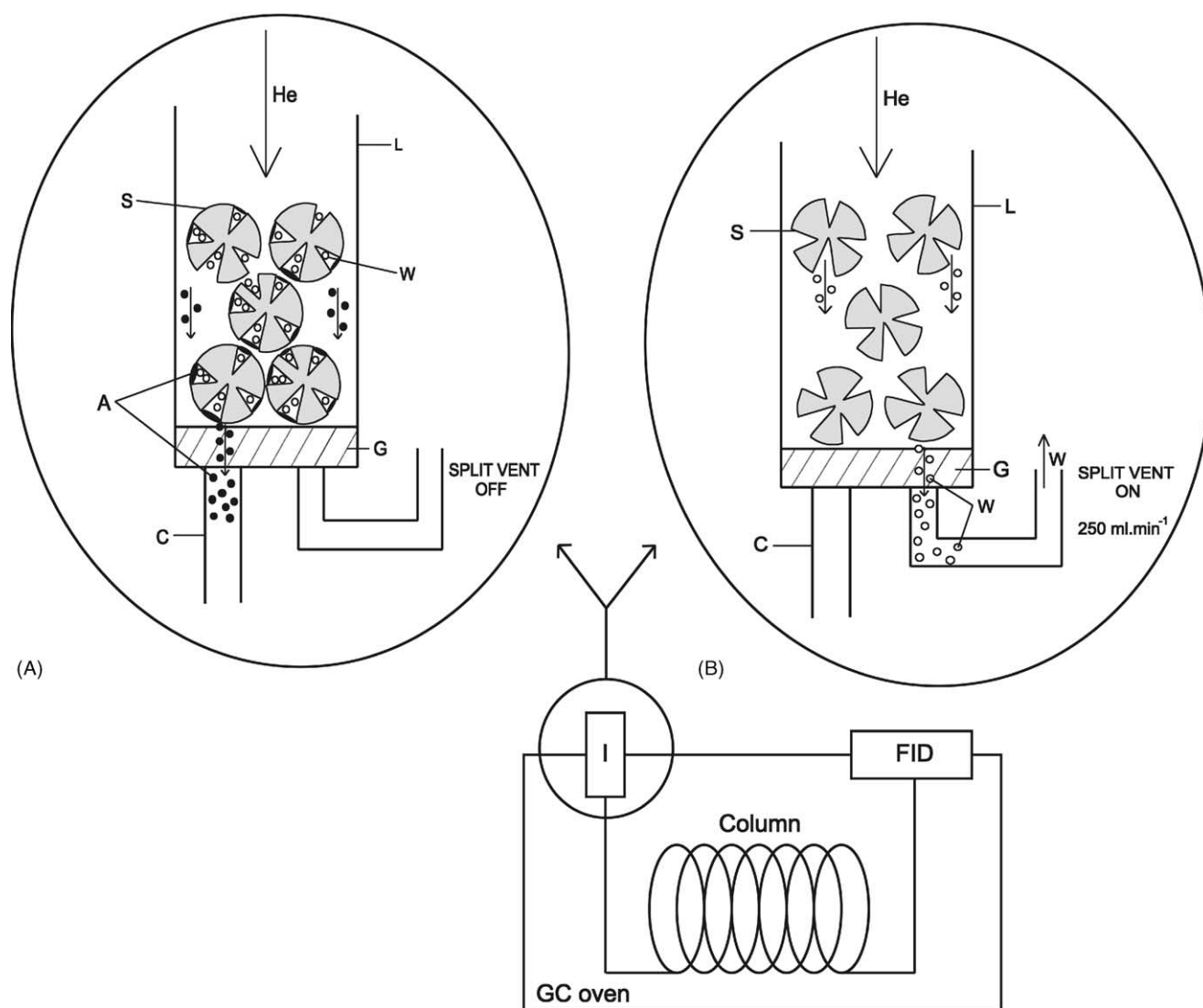

Fig. 1. Scheme of desorption process of large volume direct aqueous injection method. (A) Striping of analytes from sorbent material Chromosorb P NAW and their focusing into the capillary column. (B) Removing of water from injector using split flow. S—Chromosorb P NAW; L—injection port liner; W—water; A—analyte; G—glass wool; C—capillary column; I—injection port; FID—flame ionization detector.
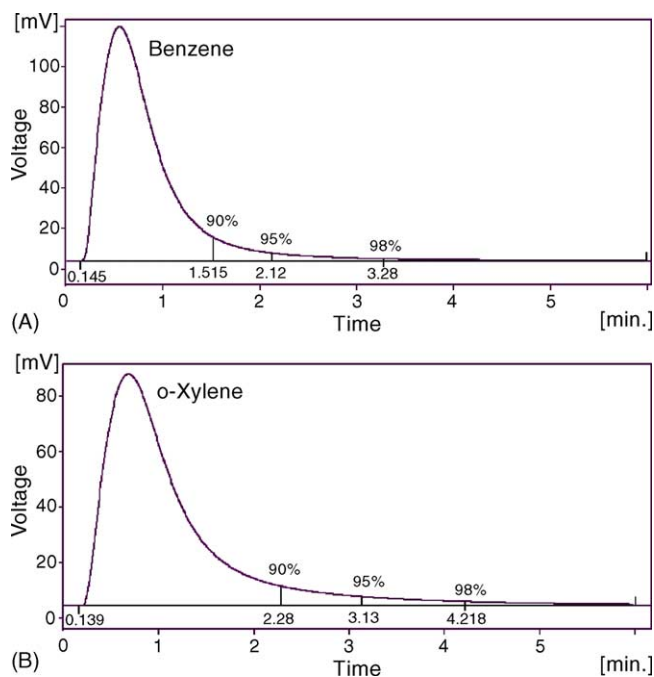
Fig. 2. The elution profile of benzene (A) and *o*-xylene (B) with the time indication where the 90, 95 and 98% of analyte is stripped from the injection port.

3.2. Optimalization test

The injection port temperature effect, injection volume effect and concentration effect were investigated using the method of experiment planning according Box-Hunter at working temperatures of the injection port in the range of 53–87 °C, injection sample volume 15.9–184.7 µl, the concentration range 12.7–147 mg l^{-1} (benzene, *o*-xylene) and the splitless mode for 6 min.

Desorbed analytes were transported into the detector through the restrictor deactivated with silanization (0.3 m × 0.1 mm) operating at the temperature of 70 °C to minimize the analyte transfer time from injector to detector, as well as to hinder of dispersion of sampling profiles. Fig. 2 shows the elution profile of studied analytes benzene and *o*-xylene with the time indication where the 90, 95 and 98% of analyte is stripped from the injection port. To reach minimal 95% recovery of individual BTEX it is necessary to keep splitless mode for 3 min.

The results of optimization test are the regression indexes b_i (Table 1) of $P = f(x_T, x_V, x_C)$ dependence which inform about influence of individual independent variables on the full quadratic model of $P = f(x_T, x_V, x_C)$ dependence:

$$y = b_0 + b_T x_T + b_V x_V + b_C X_C + b_{TV} X_T X_V + b_{TC} X_T X_C$$
$$+ b_{VC} X_V X_C + b_{TT} X_T^2 + b_{VV} X_V^2 + b_{CC} X_C^2$$

From this indexes results that the effect of injection port temperature is the most significant (the value of regression index appertaining to injection port temperature b_T is the

Table 1

The regression indexes b_i (regression indexes appertaining to injection port temperature, sampling volume, concentration, and their participation) of $P = f(x_T, x_V, x_C)$ dependence

Regression index	Benzene	*o*-Xylene
b_0	3.042	2.009
b_T	−0.505	−0.249
b_V	0	0.079
b_C	0	0
b_{TV}	−0.039	0
b_{TC}	0	0
b_{VC}	0	0
b_{TT}	0	0
b_{VV}	0	0
b_{CC}	0	0

highest, both for benzene and *o*-xylene). Less significant is the effect of injection volume indicating non-zero value of b_V (the regression index appertaining to sampling volume) for *o*-xylene and b_{TV} (the regression index appertaining to participation of injection port temperature and sampling volume) for benzene. This can be explained by undercooling of injection port at injection of large sample volume. It is indirect effect of injection port temperature on the sorption–desorption process. The concentration of analytes in the range of range 12.7–147 mg l^{-1} has no effect on the sorption–desorption process considering the zero value of the regression index appertaining to concentration b_C for both benzene and *o*-xylene.

According to this optimization the injection port temperature of 70 °C and stripping time of 3 min was chosen to reach 95% recovery of desorbed analytes and minimal penetration of water from injection port to capillary column. To determine the limits of detection and quantification was chosen the sampling volume of 250 µl, the highest volume of water sample retained in the injection port (visual determination) by used amount of Chromosorb P NAW.

3.3. Linearity of sorption–desorption process

Thirteen concentration levels (5–5000 µg l^{-1}) of BTEX were analysed performing two measurements at each concentration level for sampling volume 100 and 250 µl and 10 concentration levels (50–5000 µg l^{-1}) of BTEX for sampling volume 10 µl because of lower concentrations levels (5–20 µg l^{-1}) are below detection limits for this sampling volume. After sampling of higher concentration (5000 µg l^{-1}) the pure water was injected to investigate the memory effect. No peak was detected in the elution area of BTEX.

The change of the peak areas with the concentration of individual BTEX is linear in the listed concentration ranges, what indicate high values r^2 for all components, ranging from 0.996 for *o*-xylene and 10 µl sampling volume to 0.9999 for benzene and 100 µl sampling volume.

Table 2
The values of limits of quantification (LOQ) and detection (LOD) for large volume direct aqueous injection method

Analyte	LOD ($\mu g\,l^{-1}$)	LOQ ($\mu g\,l^{-1}$)
Benzene	0.6	2.0
Toluene	0.9	3.0
Ethylbenzene	0.9	3.0
p-Xylene	1.0	3.3
o-Xylene	1.1	3.6

3.4. Limits of determination (LOD) and quantification (LOQ)

To determine the LOD and LOQ, the measurements were performed in the concentration range of 0.5–7 $\mu g\,l^{-1}$ at sampling volume of 250 μl. For large volume direct aqueous injection method, the LOD values of BTEX are from 0.6 to 1.1 $\mu g\,l^{-1}$ and LOQ values are from 2.0 to 3.6 $\mu g\,l^{-1}$ (Table 2). The progressive trend (from benzene to *o*-xylene) of this values results from the fact that at 3 min stripping time approximately 95% of injected *o*-xylene mass penetrate to the column from injection port while for benzene it is approximately 98% (Fig. 2). The same results were reached after 200 injections of 250 μl water sample without replacement of sorbent material.

Reached LOD and LOQ values are lower by two orders than those reached by methods of direct aqueous injection and flame ionization detection before, and are below the normalized quality limit for drinking water (5, 1000, 700, and 10,000 $\mu g\,l^{-1}$ for benzene, toluene, ethylbenzene, *m*- and *p*-xylene, *o*-xylene, respectively), which makes this method suitable for monitoring of BTEX in water samples at trace levels.

This LOD and LOQ values reached by flame ionization detection are comparable with values published by Zwang et al. [3] with MS detection. In that work the injected sample volume is 25 times less and whole sampling volume is getting into the column in contrast with present work, thus the water elution as a solvent peak significantly decreases
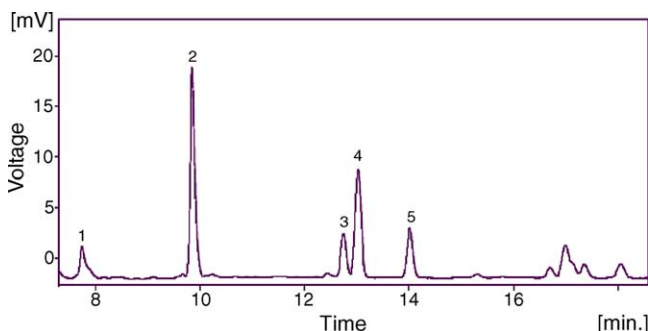
the sensitivity of MS detection in the elution area of BTEX.

3.5. Real sample

In Fig. 3 is shown the chromatogram of water sample contaminated with gasoline at sampling volume 250 μl. River sample were contaminated with gasoline at concentration 1 mg l^{-1} and determinated concentrations were 8, 45, 16, 35 and 25 $\mu g\,l^{-1}$ for benzene, toluene, ethylbenzene, *m*- and *p*-xylene, *o*-xylene, respectively. After injection of pure river water no peak was detected in the elution area of BTEX.

4. Conclusions

A new solventless method employs Chromosorb P NAW in the liner of injection port as asorbent material to retain water in the injection port while the BTEX are stripped into the column. This arrangement enables direct injection of large volume of water sample at using capillary gas chromatography to determine volatile organic compounds BTEX. The developed large volume direct aqueous injection method is suitable for the analysis of BTEX in drinking and river water samples concerning the reached detection and quantification limits. The main advantages of this method lie mainly in facility, time saving (no enrichment or pre-treatment steps are required) and lower price of analysis in comparison with any other method (purge-and-trap, SPME).

Fig. 3. Chromatogram of water sample contaminated with gasoline at sampling volume 250 μl and gasoline concentration of 1 mg l^{-1}. (1) Benzene; (2) toluene; (3) ethylbenzene; (4) *p*-, *m*-xylene; (5) *o*-xylene.

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