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DETERMINATION OF GASOLINE AND BTEX IN WATER SAMPLES BY GAS CHROMATOGRAPHY WITH DIRECT AQUEOUS INJECTION

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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.

Key words: DAI; large volume; determination BTEX; GC-FID.

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 FID detector, as well[5-7].

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 to determine BTEX analytes. 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 detection and quantification were investigated.

EXPERIMENTAL

This method use the sorption capacity of the sorbent Chromosorb P NAW (60-80 mesh) applied directly in the injection port of gas chromatograph to prevent water from penetrating into a column, but keep it adsorbed on its surface until the analytes are stripped into a column, and the residual water is purging using split flow (Fig. 1).

Using the method of experimental planning according the Box Hunter plann[8] were investigated the influence of concentration (12,7 - 147 mg.l^{-1}), volume (15,9 - 184,7 μl) and the injection port temperature (53 - 87 °C) on sorption-desorption process. These experiments were performed for benzene and *o*-xylene, the least and the most sorbed analytes, respectively, using the restrictor (0,3m x 0,1 mm) in splitless mode for 6 minutes, than split mode (250 ml.min^{-1}) and oven temperature of 70 °C. From obtained chromatograms (Fig. 2) 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.

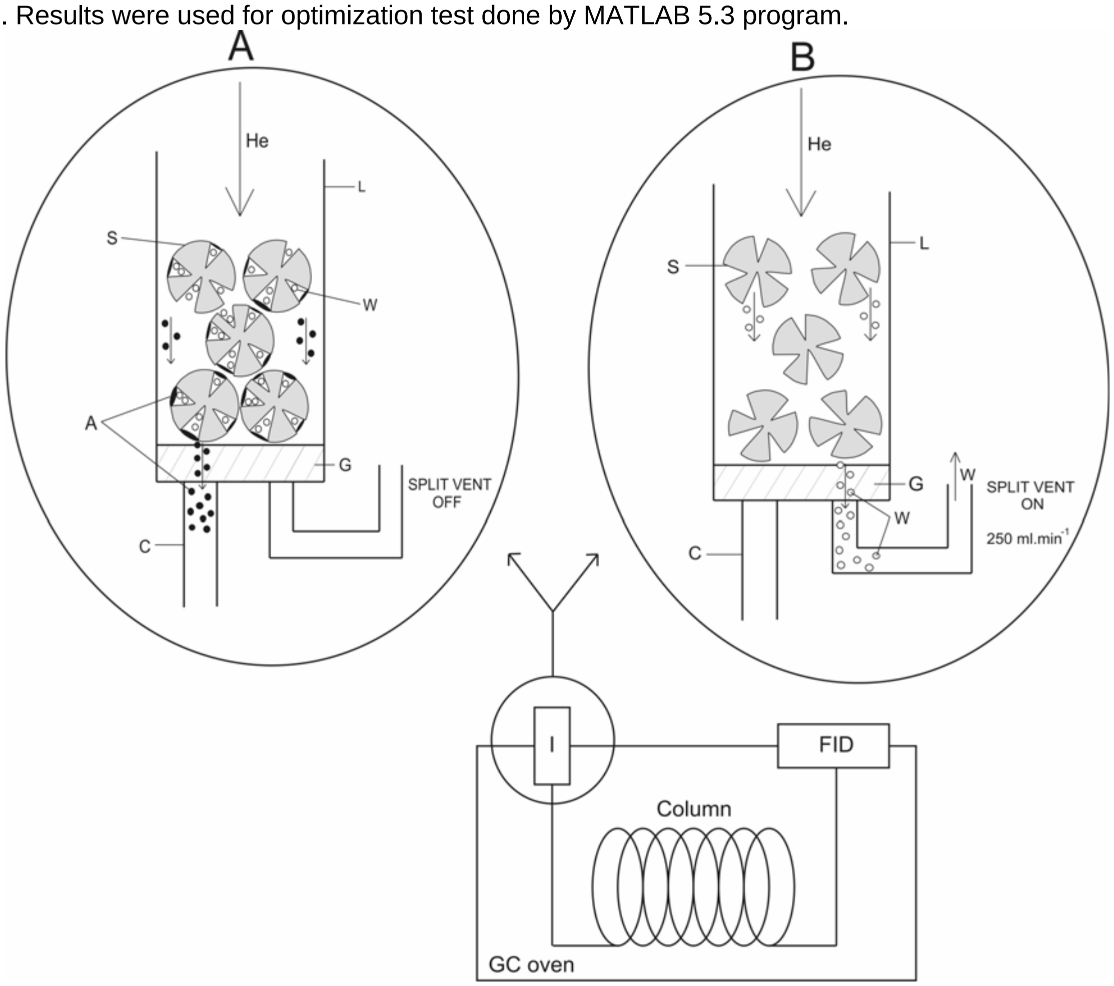
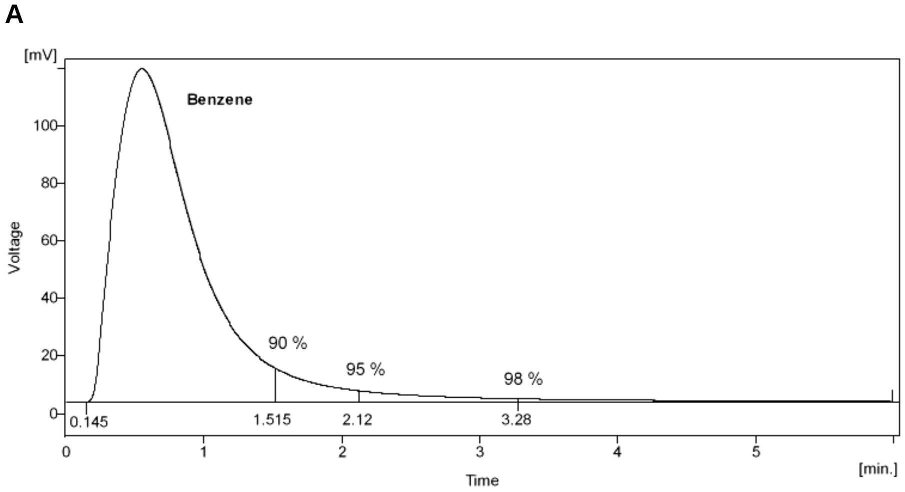


Fig. 1 Scheme of desorption process of large volume direct aqueous injection method. **A** – Striping of analytes from sorbent material Chromosorb P NAW and their focusing into the capillary column. **B** – Removing of water from injector using split flow. S – Chromosorb P NAW, L – injection port liner, W - water, A – analyte, G – glass wool, C – capillary column, I – injection port, FID – flame ionization detector.



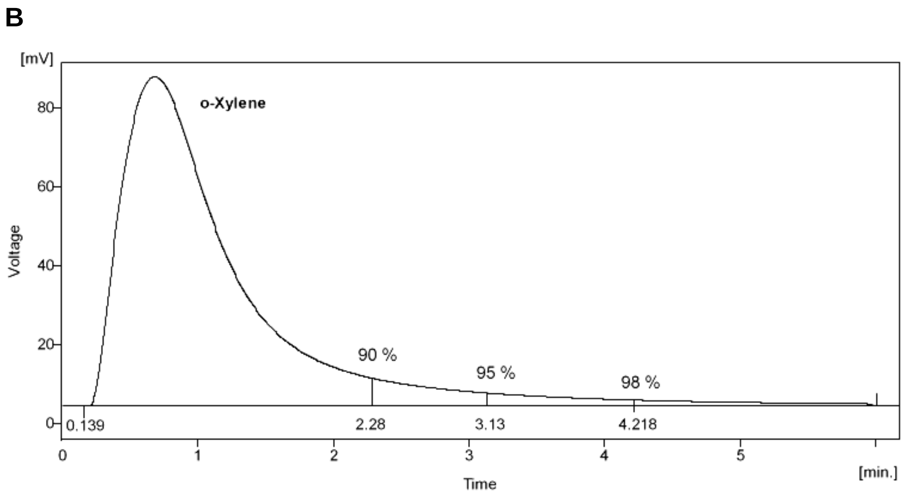


Fig. 2 The elution profile of benzene (**A**) and o-xylene (**B**) with the time indication where the 90 %, 95 % and 98 % of analyte is stripped from the injection port.

The concentration range of individual BTEX for investigation of calibration dependences was 5 - 5000 µg.l^{-1} at the sampling volume 100 and 250 µl, and 50 - 5000 µg.l^{-1} at the sampling volume 10 µl.

The sampling volume of aqueous samples for determination of detection and quantification limits with concentration of individual BTEX 0,5 - 7 µg.l^{-1} was 250 µl.

The model water sample were prepared by contamination of river water from Danube with gasoline UNI 91 (Slovnaft, Slovakia) at concentration level 1 mg.l^{-1} and the sampling volume was 250 µl.

For analytical separation of desorbed aromatic hydrocarbon standards was employed capillary column DB-1 30 m x 0,32 mm I. D. x 5 µm. Injections were made in the splitless mode for 3 minutes, than split mode (flow rate 250 ml.min^{-1}; 400 ml.min^{-1} at sampling volume of 250 µl) at injection port temperature 70 ^{o}C, and oven temperature 20 ^{o}C for 3 min, than 20 °C to 120 °C at 50 °C.min^{-1} the firs temperature ramp, and the second temperature ramp from 120 °C to 150 °C at 1,5 °C.min^{-1}.

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

RESULTS AND DISCUSSION

The optimalization test to investigation the influence of analyte concentration (*c*), sampling volume (V_{inj}) and the injection port temperature (*T*) on stripping efficiency of benzene and *o*-xylene was done. The results can be seen from graphic representation of $P=f(T, V_{inj},c)$ dependence (Fig. 3).

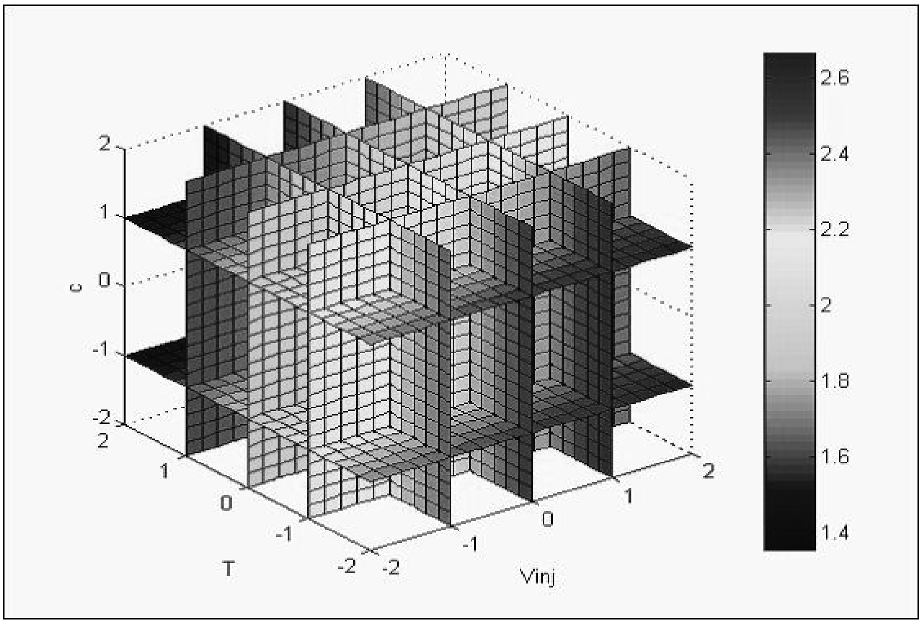


Fig. 3 Graphic representation of $P=f(T, V_{inj},c)$ dependence - full quadratic model for benzene.

The effect of injection port temperature is the most significant (major colour change along *T* axis). Less significant is the effect of injection volume (weak colour change along V_{inj} axis) what can be explained by undercooling of injection port at injection of large sample volume. The concentration of analytes in the range of 12,7 - 147 mg.l^{-1} has no effect on the sorption-desorption process (no colour change along *c* axis).

According to this optimization the injection port temperature of 70 °C and stripping time of 3 minutes 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 by used amount of Chromosorb P NAW.

The calibration dependences are linear in full concentration range (5 - 5000 µg.l^{-1}) at each sampling volume (10, 100 and 250 µl) what indicate high values of coefficients of determination r^2 for all components, ranging from 0,996 to 0,9999. After sampling of higher concentration (5 000 µg.l^{-1}) the pure water was injected to investigate the memory effect. No peak was detected in the elution area of BTEX.

For large volume direct aqueous injection method, the LOD values of BTEX are from 0,6 to 1,1 µg.l^{-1} and LOQ values are from 2,0 to 3,6 µg.l^{-1} (Table I).

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

Analyte	LOD (µg.l^{-1})	LOQ (µg.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

The progressive trend (from benzene to *o*-xylene) of this values results from the fact that at 3 minutes 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). 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; 1 000; 700 and 10 000 µg.l^{-1} for benzene, toluene, ethylbenzene, *m*- and *p*-xylene, *o*-xylene, respectively[9]), which makes this method suitable for monitoring of BTEX in water samples at trace levels.

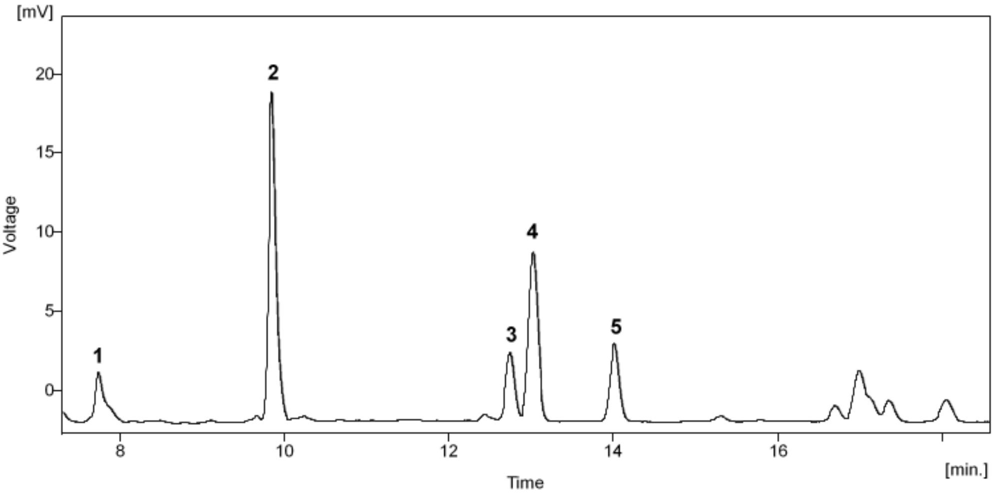


Fig. 4 Chromatogram of water sample contaminated with gasoline at sampling volume 250 µl and gasoline concentration of 1 mg.l^{-1}. 1 – benzene; 2 – toluene; 3 – ethylbenzene; 4 – *p-, m*-xylene; 5 – *o*-xylene.

In Fig. 4 is shown the chromatogram of water sample contaminated with gasoline. Determinated concentrations were 8, 45, 16, 35 and 25 µg.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.

CONCLUSIONS

A new solventless method employs Chromosorb P NAW in the liner of injection port as a sorbent 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 enrichement or pre-treatment steps are required) and lower price of analysis in comparison with any other method (purge-and-trap, SPME).

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