Needle concentrator for gas chromatographic determination of BTEX in aqueous samples

Róbert Kubinec [a,*], Victor G. Berezkin [b], Renáta Górová [a], Gabriela Addová [a], Helena Mračnová [a], Ladislav Soják [a]

[a] *Faculty of Natural Sciences, Chemical Institute, Comenius University, Mlynská Dolina CH-2, SK-842 15 Bratislava, Slovak Republic*
[b] *A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Science, Leninsky Prosp. 29, 119991 Moscow, Russia*

Abstract

A simple method of solventless extraction of volatile organic compounds (BTEX) from aqueous samples was developed and validated. A new arrangement of the full volume inside needle capillary adsorption trap (INCAT) device with Porapak Q as a sorbent material and wet alumina as a source of desorptive water vapour flow in a closed analytical system is presented. The analytical characteristics of developed device and of compared purge-and-trap (PTI) device for BTEX compounds are similar; the limits of detection as well as quantification are lower than $1\,\mu g\,l^{-1}$.
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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]. Among this enrichment of the analytes techniques is in progress, the technique of the inside needle capillary adsorption trap (INCAT) [2–10]. In this device, the sampling of a gaseous or aqueous analyzed mixture can be done by drawing a fixed volume of a sample through the sorbent placed as adsorbent layer on the interior surface or in full inside volume of stainless steel needle. The volatile analytes sorbed on the sorbent, which can be adsorbent or liquid coated onto a support, are thermally desorbed in the heated injection port of a gas chromatograph and then directly swept by the carrier gas into the capillary column for analysis. Procedure of solid phase dynamic extraction of organics using a wall-coated syringe needle was automated [8].

The main advantages of INCAT device lie in the simple methodology and easiness and rapidity of the analyses [5].

The drawbacks involve the fact that the samples collected can be not particularly large, the desorption temperature is limited by that of the gas chromatographic injection port, and the elution zones of analytes are slightly dispersed [5]. Other problems consist in competitive effects and variation in sampling efficiencies for the different analyzed compounds as the result of the low capacity of the sorbent [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 is for benzene 1, toluene 50 and for xylene $100\,\mu g\,l^{-1}$, respectively [11]. The analysis of BTEX in aqueous samples is usually achieved by purge-and-trap (PTI) gas chromatography (GC) [12]. The aim of this work was to develop a cheaper device with adsorbent inside of the full volume of stainless steel needle suitable for the pre-concentration BTEX from aqueous samples. The present paper describes a new arrangement of the full inside volume needle capillary adsorption trap device with Porapak Q as a sorbent material and wet alumina as a source of desorptive water vapour flow in a closed analytical system. The experimental parameters as temperature of sample, temperature of GC injection port, effect of sample flow rate as well as of volume sample and concentration of analytes on analyte recovery were investigated.

* Corresponding author. Tel.: +421-2-60296-330;
fax: +421-2-65429-064.
E-mail address: kubinec@fns.uniba.sk (R. Kubinec).

2. Experimental

2.1. Materials

Porapak Q 0.15–0.18 mm with a specific surface area of $550\,m^2\,g^{-1}$ and aluminum oxide with a grain size of 0.2–0.4 mm as packed materials for needle concentrator were purchased from Waters Assoc. Inc. (Framingham, MA, USA) and Merck (Darmstadt, Germany), respectively. Standards BTEX (benzene, toluene, ethylbenzene, *p*-xylene and *o*-xylene) were from Slovak Institute of Metrology (Bratislava, Slovakia), and methanol (gradient grade) from Merck (Darmstadt, Germany).

Stainless steel needles (cannula) 90 mm long with an outer diameter (o.d.)/inner diameter (i.d.) of 1.3/1.1 mm, and 1.1/0.9 mm were from Nissho (Osaka, Japan), and from this material were prepared also O-rings (3 mm × 1.1 mm o.d./0.9 mm i.d.). Stainless steel frits ($20\,\mu m$ porosity and 0.16 mm depth) were from Carlo Erba (Milano, Italy), glass syringe for water sampling (volume 5 ml) from Graf Fortuna (Wertheim, Germany), and viton tubing 20 mm × 5 mm o.d./0.9 mm i.d. from Masterflex (Vernon Hills, IL, USA).

Restrictor as an uncoated deactivated silica capillary column of 0.7 m × 0.1 mm from Caco (Bratislava, Slovakia) was used for investigation of the sorption–desorption process of analytes in INCAT device, and a DB-1 30 m × 0.53 mm i.d. × $3\,\mu m$ (J&W Scientific, Blue Ravine Road, Folsom, USA) column was employed for analytical separation of desorbed aromatic hydrocarbon standards.

2.2. Sampling

2.2.1. INCAT

Drinking water samples (500 ml) were spiked with $100\,\mu l$ of methanol standard solution containing 8–1000 ng μl^{-1} of each BTEX. Concentration of each BTEX in drinking water models were 1.6, 3.12, 6.25, 12.5, 25, 50, 100, 200 $\mu g\,l^{-1}$. Aqueous samples of concentration $10\,mg\,l^{-1}$ (volume of 100 ml) for investigating the adsorption–desorption processes in INCAT device were prepared by adding of 1 mg of aromatic standards. Water sample was extracted by INCAT device and propelled by glass syringe, or HPLC pump (Laboratorní Pøístroje, Praha, Czech Republic) to maintain the precision measurements of flow rate ranges (0.5–9 ml min^{-1}) and volume ranges (0.1–50 ml). Needle concentrator was termostated in water bath (W6, Grant Instruments, Cambridge, England) by temperature ranges 5–95 °C with precision ±0.5 °C.

2.2.2. PTI

The PTI device (Chrompack, Middelburg, The Netherlands) was used as an comparative automatic stripping and pre-concentration system of volatiles from aqueous matrices. The PTI unit consisted of a 5 ml stripping vessel, a water condenser cooled with ethanol (−10 °C), a fused-silica trapping capillary tube (30 cm × 0.53 mm i.d.; film thickness 2.65 μm) coated with an immobilized methylsilicone stationary phase (SE-54) and an oven that heats the trap.

The water sample was purged with helium (99.996% purity) (MG Tatragas, Bratislava, Slovak Republic) at 30 ml min^{-1} during 10 min. The volatiles were trapped in the trapping capillary tube cooled to −100 °C using liquid nitrogen (MG Tatragas, Bratislava, Slovak Republic). Subsequently, the volatiles were thermally desorbed (220 °C, 2 min) into the DB-1 analytical capillary column. The PTI operation conditions were optimalised in our previous work [13].

2.3. GC analysis

The GC measurements were performed on gas chromatograph HP 5890 SERIES II Hewlett-Packard (Avondale, USA) equipped with flame ionization detector (FID) and a split–splitless injector, and a CP 9000 gas chromatograph (Chrompack, Middelburg, The Netherlands) equipped with FID and a PTI device. The carrier gas was helium with a pressure of 30 kPa in the injection port and in the PTI device. The detectors temperature was maintained at 250 °C. Injections for investigation of adsorption–desorption processes of INCAT device were made in the split mode (flow rate 200 ml min^{-1}) at various temperatures of injection port in the range of 120–320 °C, and oven temperature 250 °C for each analyte. Injections for separation of desorbed aromatic standards from INCAT device were made in the splitless mode (closed split valve during analysis) at injection port temperature 280 °C, and oven temperature 40 °C and heated quickly 10 °C min^{-1} to 160 °C.

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

For investigation of INCAT device 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 co-elutate given as sum of *m*- and *p*-xylene because these isomers show similar recovery and response. In the case of required individual, analyze of these isomers is necessary by use other GC column which separates *m*- and *p*-xylenes.

2.4. Method validation

The validation process of the method was performed according to EURACHEM guidelines [14,15]. Detection (y_D) and quantitation (y_Q) limits were expressed as signals based on the mean blank ($\bar{x}_b$) and the standard deviation of blank responses (s_b):

$$y_D = \bar{x}_b + 2ts_b, \qquad y_Q = \bar{x}_b + 10s_b$$

where t is the constant of the Student's *t*-test distribution (one-tailed) depending on the confidence level (a 95% confidence interval (CI) level was chosen) and degrees of freedom (d.f.). The x_b and s_b were calculated by performing 10 blank measurements. The concentration values of the detection limit (LOD) and quantitation limit (LOQ) were

obtained by projection of the corresponding signals y_D and y_Q through a calibration plot $y = f(x)$ onto the concentration axis. Linearity was verified up to two orders performing three measurements at each concentration level. Linearity was confirm by performing Mandel's fitting test.

3. Results and discussion

3.1. INCAT design

A new INCAT device with adsorbent inside of the whole volume of stainless steel needle was developed for the pre-concentration of trace volatile organic compounds (BTEX) from aqueous samples. As can be seen from Fig. 1, it comprises a stainless steel needle N, stainless steel O-ring O, stainless steel frits F, in laboratory prepared shut-off micro valve V with stainless steel body and viton tubing T, adsorbent Porapak Q 0.15–0.18 mm (50 mm length of needle) P, and alumina 0.2–0.4 mm (7 mm length of needle) A.

Fig. 2 represents single steps of adsorption and desorption of BTEX from INCAT device. Aqueous sample is passed through the INCAT device by means of a syringe with 5 ml volume at speed about 1 ml min^{-1} (Fig. 2A). Subsequently, the INCAT device is flushed by ca. 0.5 ml of air to remove residual water (approximately of 50 μl) (Fig. 2B) at room temperature. Then, the valve is closed and the INCAT device is introduced to GC injection port with 1 ml liner in the splitless mode at 280 °C. Adsorbed analytes are thermally desorbed from Porapak Q and displaced to the injection port with gradually purging water steam formed by evaporation of water (approximately of 9 μl determined by weighing of alumina sorbent). Various materials were tested for the water reservoir in needle concentrator, e.g. silica and molecular sieve, but the alumina (see Section 2) was found to be most suitable. Desorbed analytes are separated by capillary gas chromatography and detected by FID detector (Fig. 2C). Once the analyze is finished the valve on INCAT device is open and residual organic compounds are removed by stream of helium with flow of 70 ml min^{-1} within 2 min (Fig. 2D).
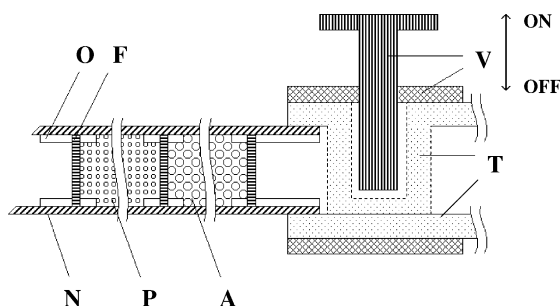

Fig. 1. Scheme of INCAT system. (N) stainless steel needle; (O) stainless steel O-ring; (F) stainless steel frits; (P) adsorbent Porapak Q; (A) adsorbent alumina; (V) shut-off micro valve with stainless steel body; and (T) viton tubing.
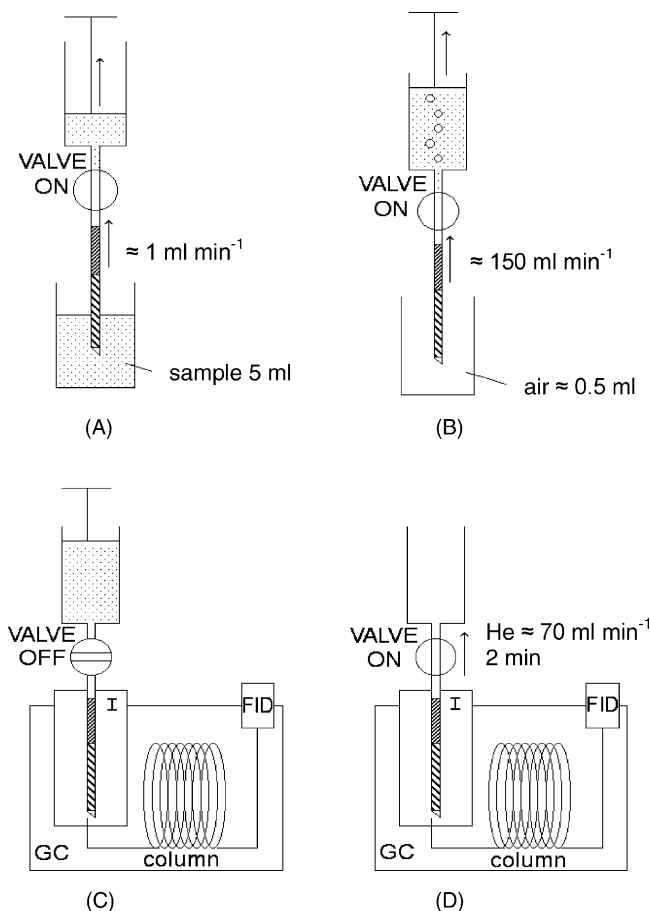

Fig. 2. Scheme of sorption and desorption process of INCAT device. (A) Sampling of aqueous samples; (B) removing of residual water; (C) desorption; (D) cleaning.

In contrast with the INCAT systems published previously, the proposed needle concentrator is characteristic by closed sorption–desorption system in which thermally desorbed analytes are with the assistance of water vapors repelled to the injection port of gas chromatograph without additive make-up gas. This modification allows using this needle concentrator for each type of gas chromatograph with split–splitless injector without any modification.

3.2. Time, recovery and repeatability of desorption process

The time, recovery and repeatability of desorption process of BTEX in INCAT device were studied at working temperatures of the injection port in the range of 120–320 °C, and split mode with the split flow rate of 200 ml min^{-1}. The number of replicated analyses for each temperature were three.

Desorbed BTEX were transported into the detector through the restrictor deactivated with silanization (0.7 m × 0.1 mm) operating at the temperature of 250 °C to minimize the analyte transfer time from injector to detector, as well as to hinder of dispersion of sampling profiles. Fig. 3 shows the dependence of peak area of o-xylene, the
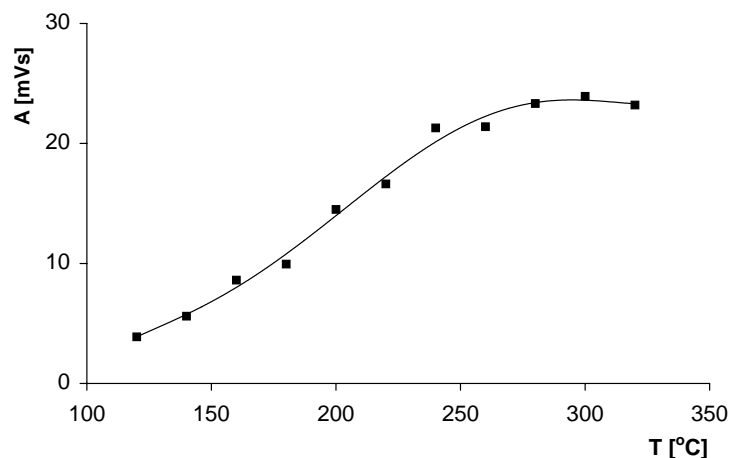
Fig. 3. The dependence of peak area of *o*-xylene on the temperature of injection port. The number of measurements for each temperature were three.

most sorbed component of BTEX, on the temperature of injection port at sample volume of 5 ml and concentration 10 mg l^{-1}. It can be seen that peak area of *o*-xylene increases with the temperature until approximately 250 °C is achieved. It means that the constant amount of desorbed *o*-xylene is obtained above injector temperature of 250 °C.

Fig. 4 shows the dependence of relative standard deviation of *o*-xylene peak area on the temperature of injection port. The values of relative standard deviations of peaks area is near constant (approximately 2%) above the temperature of 250 °C. Higher relative standard deviations at lower temperatures, e.g. 85% at 120 °C, are caused mainly by incomplete desorption of *o*-xylene, and partly by variance of needle position in injector port which can cause different thermal transfer between the injector port and the needle. Dependences of relative standards deviations of benzene, toluene,

ethylbenzene and *p*-xylene peaks areas on the temperature of injection port were similar.

3.3. Recoveries, repeatability, linearity and sample capacity of INCAT sorption–desorption process

The recoveries and their repeatability, FID response linearity and sample capacity of INCAT sorption–desorption process were studied at injection port temperature of 280 °C using of capillary column DB-1. In Table 1 are listed the recoveries of BTEX from model water sample at concentration 200 μg l^{-1} and flow 1 ml min^{-1} at different temperatures of extraction. From this table, it is evident that the recoveries of BTEX, ranging from 96 to 102% with the values of relative standard deviation within 0.1–4.2%, change at relatively narrow extent in the extraction temperatures range from 5 to
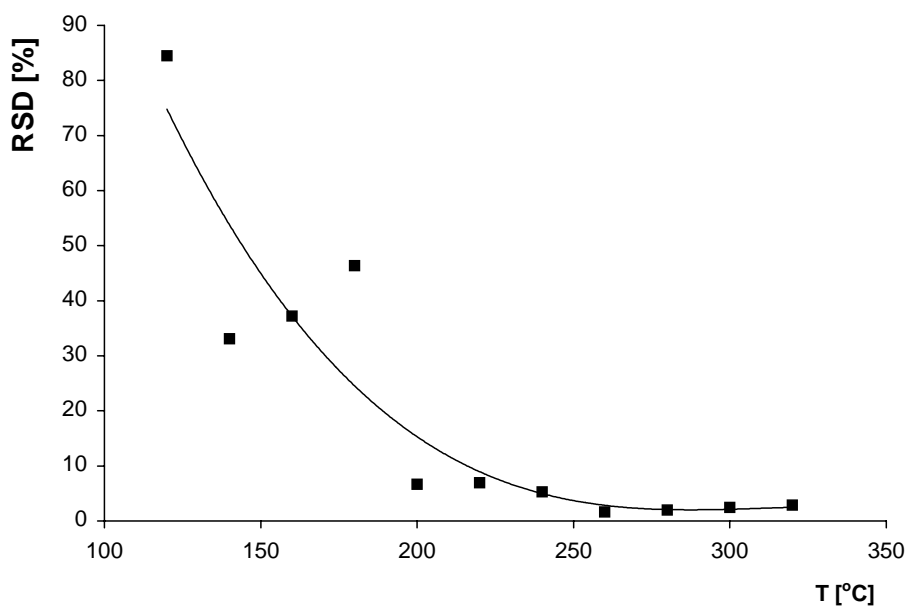

Fig. 4. The dependence of relative standard deviation of *o*-xylene peak area on the temperature of injection port. The number of measurements for each temperature were three.

Table 1

The recoveries (*R*%) of BTEX from water and their relative standard deviations (R.S.D.%) at concentration $200\,\mu g\,l^{-1}$ and flow $1\,ml\,min^{-1}$ at different temperatures of extraction

T (°C)	*R*% (R.S.D.%)				
	Benzene	Toluene	Ethylbenzene	*p*-Xylene	*o*-Xylene
5	97 (0.1)	100 (0.8)	102 (1.4)	98 (0.1)	96 (0.8)
25	98 (2.4)	99 (0.2)	99 (1.9)	99 (0.8)	97 (1.4)
40	98 (0.9)	100 (1.6)	101 (4.2)	98 (0.8)	96 (3.2)
60	98 (0.6)	99 (0.5)	99 (0.1)	99 (2.4)	101 (1.4)
80	96 (1.8)	97 (0.9)	98 (1.1)	98 (3.0)	98 (1.4)
95	95 (0.1)	96 (0.1)	95 (0.5)	93 (2.7)	95 (1.4)

The numbers of measurements for each temperature were three.

Table 2

The recoveries (*R*%) of BTEX from water and their relative standard deviations (R.S.D.%) for concentration of $200\,\mu g\,l^{-1}$, in dependence on flow rate of the sample through the INCAT device at temperature 25 °C

Flow (ml min^{-1})	*R*% (R.S.D.%)				
	Benzene	Toluene	Ethylbenzene	*p*-Xylene	*o*-Xylene
0.5	99 (2.6)	99 (1.9)	97 (0.6)	99 (0.2)	97 (0.9)
1	98 (2.4)	99 (0.2)	99 (1.9)	99 (0.8)	97 (1.4)
2	97 (0.9)	97 (2.3)	96 (1.4)	96 (3.4)	96 (2.6)
4	98 (2.7)	98 (2.4)	97 (2.9)	97 (1.8)	96 (2.4)
6	91 (2.1)	92 (0.8)	90 (2.5)	90 (3.2)	89 (3.6)
9	82 (1.9)	83 (1.9)	81 (3.0)	84 (2.0)	81 (3.8)

The numbers of measurements for each sample flow rate were three.

80 °C. The small decrease of recovery was found at 95 °C, nevertheless at this temperature the recovery of each BTEX does not decrease under the 93%.

In Table 2 are listed the recoveries of BTEX for concentration $200\,\mu g\,l^{-1}$ at temperature of 25 °C, in the dependence on sample flow rate through the needle concentrator. It is evident that the recoveries are near constant (96–99%) in the sample flow rate range of 0.5–$4\,ml\,min^{-1}$. The decrease of recovery is noticeable at higher sample flow rates of 6 and $9\,ml\,min^{-1}$, when the recovery goes down up to 81%.

Eight concentration levels of BTEX were analysed performing three measurements at each concentration level. In Table 3 are listed the recoveries of BTEX, relative standard deviations of recoveries, and coefficients of determination at concentrations 1.6–$200\,\mu g\,l^{-1}$. From Table 3, it follows that the change of the peak areas with the concentration of individual BTEX is linear in the concentration range of 1.6–$200\,\mu g\,l^{-1}$, what indicate values F_{cal} and F_{crit} from Mandel's test for all components analysed using INCAT device. The recoveries for each analyte in full range of studied concentrations are from 86% (*o*-xylene at concentration $3.1\,\mu g\,l^{-1}$) to 105% (toluene at concentration $1.6\,\mu g\,l^{-1}$).

The relative standard deviations are ranging from 0.2 to 21.0% and increase with decreasing the concentration of analytes.

The dependence of peaks area of BTEX on volume samples at concentration $200\,\mu g\,l^{-1}$, flow of $1\,ml\,min^{-1}$, and temperature 25 °C are linear for all tested components, what indicate values F_{cal} and F_{crit} from Mandel's test in the broad range of sampled volumes 0.1–$50\,ml$. The problem occurs when the volumes lower than $0.1\,ml$ are sampled looking on the relative small internal volume of INCAT device ($120\,\mu l$). The sampling of volume higher than $50\,ml$ at concentration $200\,\mu g\,l^{-1}$ results in overloaded peaks what leads to the incomplete separation of some compounds. Obtained results show on high sorption capacity of the developed INCAT device, the limiting factor for the determination of BTEX at higher quantities of analytes is the capacity of used capillary gas chromatographic column.

3.4. Comparison of LOD and LOQ values of BTEX obtained by INCAT and PTI methods

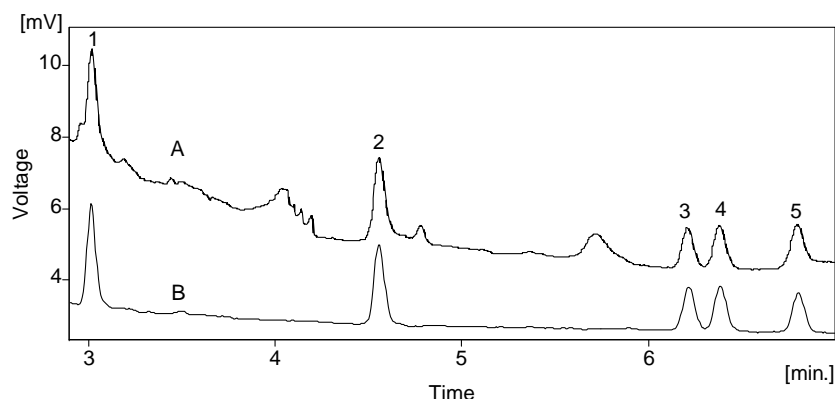In Fig. 5 are shown the chromatograms of BTEX compounds at concentration of $1\,\mu g\,l^{-1}$ individual aromatics

Table 3

The values of the peak areas (*A*) of BTEX, their recoveries (*R*%) and relative standard deviations of recoveries (R.S.D.%), the coefficients of determination (r^2), calculated (F_{cal}) and critical (F_{crit}) values of Mandel's test at concentrations (*C*) 1.6–$200\,\mu g\,l^{-1}$ using INCAT device

C (μg l^{-1})	*A*(mVs), *R*% (R.S.D.%)									
	Benzene		Toluene		Ethylbenzene		*p*-Xylene		*o*-Xylene	
1.6	5.92	103 (2.8)	5.92	105 (7.3)	5.07	99 (13.4)	6.19	101 (7.1)	5.90	95 (21.0)
3.12	10.0	87 (8.7)	10.5	93 (5.3)	10.5	102 (13.5)	10.8	88 (1.9)	10.7	86 (16.2)
6.25	21.9	95 (1.6)	22.1	98 (8.6)	20.4	99 (7.9)	21.1	86 (8.3)	24.3	98 (6.4)
12.5	43.8	95 (4.2)	42.3	94 (2.8)	38.9	95 (1.7)	43.3	88 (2.2)	48.3	97 (4.7)
25	86.4	94 (2.2)	86.5	96 (2.5)	82.0	100 (2.8)	90.9	93 (2.3)	96.5	97 (1.2)
50	173	94 (3.3)	171	95 (2.2)	159	97 (1.7)	191	98 (0.9)	193	97 (3.1)
100	373	101 (0.9)	356	101 (1.4)	336	102 (1.8)	395	101 (1.3)	404	102 (2.1)
200	720	98 (2.4)	715	99 (0.2)	650	99 (1.9)	775	99 (0.8)	769	97 (1.4)
r^2	0.9995		0.9997		0.9997		0.9998		0.9994	
F_{cal}	0.77		0.07		1.99		1.13		7.54	
F_{crit}	12.25		12.25		12.25		12.25		12.25	

The numbers of measurements for each concentration were three.

Fig. 5. Chromatograms of BTEX at concentration of $1\,\mu g\,l^{-1}$. (1) Benzene; (2) toluene; (3) ethylbenzene; (4) *p*-xylene; (5) *o*-xylene. (A) INCAT method; (B) PTI method.

Table 4
The values of limits of quantification (LOQ) and detection (LOD) for INCAT and PTI methods

Limits ($\mu g\,l^{-1}$)	Benzene	Toluene	Ethylbenzene	*p*-Xylene	*o*-Xylene
LOQ[a]	0.80	0.83	0.43	0.43	0.46
LOD[a]	0.38	0.39	0.20	0.20	0.22
LOQ[b]	0.23	0.26	0.33	0.33	0.36
LOD[b]	0.11	0.12	0.16	0.16	0.17

  [a] INCAT.
  [b] PTI.

obtained by INCAT and PTI methods. It is evident that the concentration level of $1\,\mu g\,l^{-1}$ at sample volume of 5 ml is above the detection limit for all BTEX compounds for both methods, INCAT and PTI as well. The raising background of INCAT analysis is caused by impurities from water and methanol, eventually by decomposition products from IN-CAT device, and by co-elution of water as a solvent peak with benzene and toluene.

For INCAT method, the limits of detection values of BTEX are from 0.20 to $0.39\,\mu g\,l^{-1}$ and for PTI method are in the range from 0.11 to $0.17\,\mu g\,l^{-1}$ (Table 4). The LOD value 3.5 times higher for benzene and 3.2 times higher for toluene achieved by INCAT method in comparison with those achieved by PTI method are caused by co-elution of these compounds with water as a solvent peak. The results given in Table 4 confirm that the competitive effects and variation in sampling efficiences obtained for lighter aromatic hydrocarbons (benzene, toluene) on graphite adsorbent [7] and polydiphenylphtalid [9] are eliminated in this developed INCAT device.

3.5. Conclusions

A new arrangement of the full inside volume needle capillary adsorption trap device with Porapak Q as a sorbent material and wet alumina as a source of desorptive water vapour flow enable high efficiency and repeatabil-

ity of adsorption and desorption of trace quantities of BTEX from water matrix. The developed INCAT device is suitable for the analysis of BTEX in drinking and waste water samples. The limit of detection as well as limit of quantification of BTEX compounds analysed in IN-CAT device is comparable with those for purge-and-trap technique. The main advantages of INCAT device in comparison with PTI device lie mainly in substantially lower price of analysis and the possibility of sampling directly in the field. The drawbacks involve the co-elution of benzene and toluene with water as a solvent peak causing slightly worse detection and quantification limits in comparison with ethylbenzene and xylenes. Other potential problem is the rise in decomposing products of Porapak Q [16].

Acknowledgements

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