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HIGH-SENSITIVE GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC DETERMINATION OF ESTERS OF *O*-PHTHALIC ACID IN WATER WITH LIQUID-PHASE MICROEXTRACTION

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ABSTRACT

It has been shown that the ultrasound-assisted emulsification-microextraction is an efficient method for preconcentration of esters of *o*-phthalic acid. Application of extract capillary collection solved the problem of low-density (“light”) extractant sampling. The loss of the extractant during extraction due to evaporation and dissolution were measured and they were statistically insignificant. Rayleigh distillation method has been proposed for purification of the extractant. It has been found that leaching of *o*-phthalates into the carrier gas flow from chromatographic septum is the source of systematic errors in impurities determination. The relative expanded uncertainty of *o*-phthalates determination is at the level of 12–39 %. The limits of detection of esters of *o*-phthalic acid achieved are at the level of 4×10^{-6}–1×10^{-5} mg L^{-1} and are highly competitive with the best world results.

KEYWORDS: Microextraction, preconcentration, ultrasonic dispersion, esters of *o*-phthalic acid, detection limit, trueness conformation.

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INTRODUCTION

o-Phthalic acid esters (*o*-phthalates) are quite toxic compounds. The maximum permissible concentration (MPC) of *o*-phthalates in water for beverage production is 3–0.008 mg L^{-1} [1]. Therefore, it is necessary to use high-sensitive methods with preconcentration for detection of these compounds. The liquid-liquid extraction is a widespread method for preconcentration. The traditional liquid-liquid extraction (macroextraction) has a number of significant disadvantages: the use of too large volume of expensive organic solvents, problems with automation. The utilization of toxic extractants (their volumes can achieve tens and hundreds of ml) is a serious problem. These disadvantages were removed by the method of liquid microextraction where the amount of the extractant is reduced by 3-4 order and it does not exceed 50-100 µL [2, 3]. The efficiency of the liquid-liquid extraction is characterized by the recovery *R* and the enrichment factor *K*. The main purpose of preconcentration is decreasing of the impurities detection limit. The limit of detection is reduced by increasing the signal/noise ratio, the latter increases with the degree of extraction of the analyte. Fig 1 shows the dependence of extraction recoveries *R* and enrichment factors *K* on the ratio of water and extractant volumes V_w/V_o for partition coefficients of *o*-phthalates *D* [4, 5] and the dependence of *R* and *K* on extractant volumes V_o , if V_w = 3 ml (as in this work). Small values of *R* explained by the relatively not very large values of *D* [4, 5].

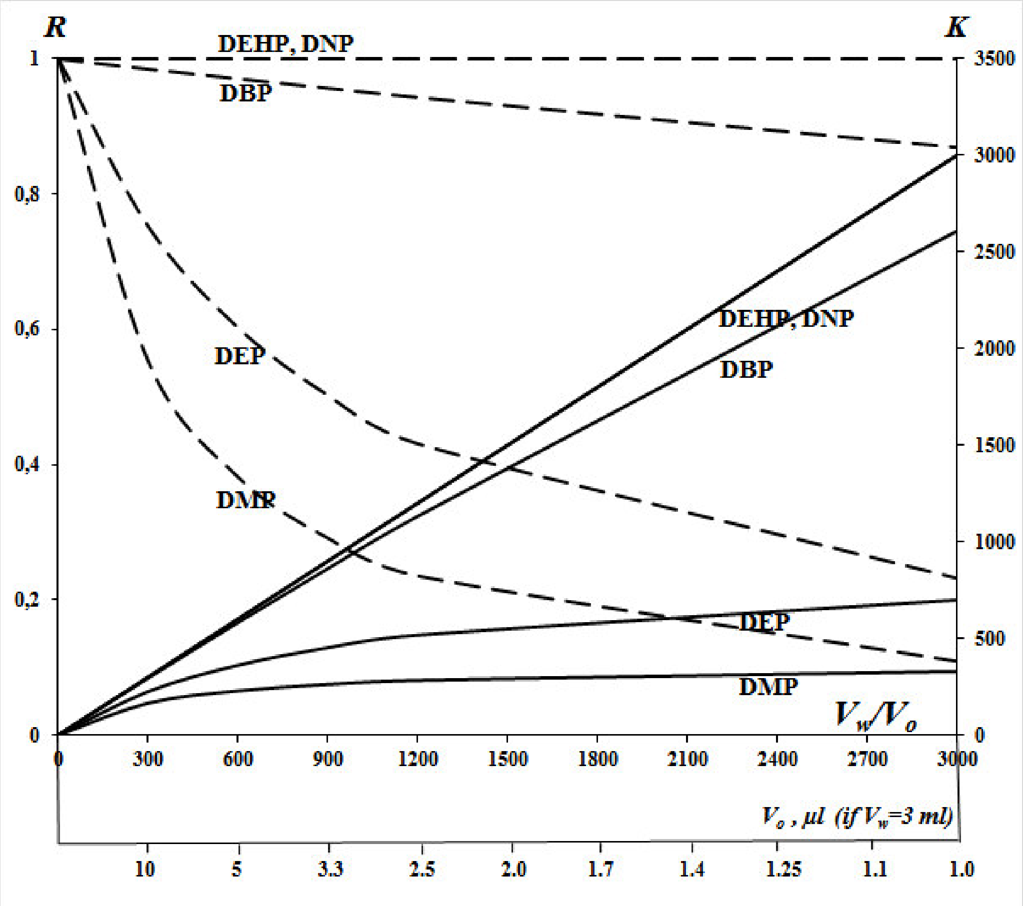

Figure 1

The dependence of enrichment factors K (full line) and extraction recovery R (dotted line) on ratio of water and extractant volumes V_w/V_o and on extractant volumes V_o, if water volume V_w=3 ml: DMP – dimethyl phthalate, D = 372; DEP – diethyl phthalate, D = 912; DBP – di-n-butyl phthalate, D = 19953; DEHP – di(2-ethylhexyl) phthalate, D = 4897788; DNP dinonyl phthalate, D = 22908676.

As it can be seen from Fig 1, the increase in extractant volume V_o from 1 to 10 µL led to the increase in the recovery of DMP and DEP by 4.5 times. It leads to the same increase in the signal/noise ratio and to improvement of the limit of detection. Thus, the recovery is a more informative parameter of microextraction preconcentration. It is necessary to strive for complete extraction of the analyte within the permissible volumes of extractant and to inject all recovered extract into the analytical instrument. Nevertheless, large volume injection for *o*-phthalates determination is used only in HPLC analysis and is very rare in GC one. Currently, the most effective liquid microextraction is connected with the dispersion of the extractant. Different methods of dispersing have been proposed for determination of *o*-phthalic esters: dispersing with the third component [6], the vortex dispersion [7], air-assisted dispersion [8], and ultrasound dispersion [9, 10]. The lowest detection limits at the level 5×10^{-6}–1.3×10^{-4} mg·L^{-1} were obtained with ultrasonic dispersion. Unreliable results of the *o*-phthalates determination are very probable since these compounds are widespread and can penetrate into the analyzed sample even from the air [11]. In this paper the method of microextraction with ultrasonic dispersion of low-density extractant and capillary collection of extract has been investigated for preconcentration of *o*-phthalic acid esters, the sources of systematic errors of impurities determination have been identified and uncertainty of the analysis has been calculated.

MATERIALS AND METHODS

1. Instrumentation and reagents

DMP GOST 9657-61, DEP TU 6-09-3663-74, DBP GOST 2102-78, DEHP GOST 8728-88, DNP TU 6-09-2800-75. *n*-Octane TU 6-09-3748-74 was used as an extractant. *n*-Octane has been additionally purified by Rayleigh distillation method [12]. *n*-Octane meets the requirements of the extractant for microextraction. It has low solubility in water of 0.66 mg L^{-1} and low volatility (T_{boil}=125.7°C) [13]. Besides, *n*-octane does not cause difficulties for gas chromatographic detection of *o*-phthalates. The volume of extractant was 10 µL. Sodium chloride GOST 4233-77 was used as a salting additive. The solutions 3×10^{-4}–1 mg L^{-1} of each *o*-phthalate were prepared in double-distilled water and purified *n*-octane by sequential dilution. Since the *o*-phthalates are slightly soluble in water, the solutions were prepared using ethanol GOST 1830087 purified by Rayleigh distillation [14]. The solutions were prepared in glass ampoules with ground stoppers. The mass of substances was controlled within 0.0001 g using the analytical balance Shimadzu aux 220. Ultrasonic bath model GY 3560; centrifuge CLN-2 (MRTU 42-1742-63 N2509); chromatographic septa: Agilent 5080-8894, Agilent 5183-4759-S, Agilent BTO 5183-4757-S, SGE AUTO-SEP Pkt.25 BATCH CO-01, Thermo-Finnigan 31303211, Thermo-Finnigan 313G3211-1, Agilent High Pressure Merlin Microseal septum; vials Agilent 5182-0714; glass ampoules of 5 ml with ground-glass stoppers; microsyringe HAMILTON 701-N of 10 µL; glass syringe of 5 ml; installation for the Rayleigh distillation [14]. Focus DSQ II and Agilent 5973N gas chromatograph-mass spectrometers with quadrupole mass analyzer were used for determination of impurities. Impurities detection was carried out in the selective ion scan lines of mass spectrum characterized by the maximum signal/noise ratio. Scanned ions: *m/z* 163 – DMP, *m/z* 149 – DEP, DBP, DNP, DEHP. Chromatographic separation was accomplished with TR-5ms fused-silica capillary column (30 m × 0.25 mm I. D., 0.25 µm film thickness) coated with 5%-biphenyl-95%-dimethylsiloxane stationary phase. Helium 60 (TU 0271-011-45905715-02) was employed as a carrier gas at flow rate of 1 ml min^{-1}. The GC oven temperature was as follows: the initial temperature was 50°C for 1 min, 40°C min^{-1} to 120°C min^{-1}, then 10°C min^{-1} to 280°C and was held for 10 min. The temperature of the transfer line was set at 300°C. We used the programmable temperature vaporizer. The initial temperature of the inlet was 127°C (to prevent a condensation of *n*-octane). After solvent evaporation, the vaporizer temperature was increased to 170°C. The first minute of injection was splitless, and then the ratio of split flow was 1:10.

2. Ultrasound-assisted emulsification-microextraction (USAEME)

The preconcentration was carried out in centrifuge tube. The tops of tubes were made as the calibrated capillary with a diameter of 1.4 ± 0.05 mm. The capillary tube was designed to collect the extract [15, 16]. The scheme of preconcentration method is shown in Fig 2.

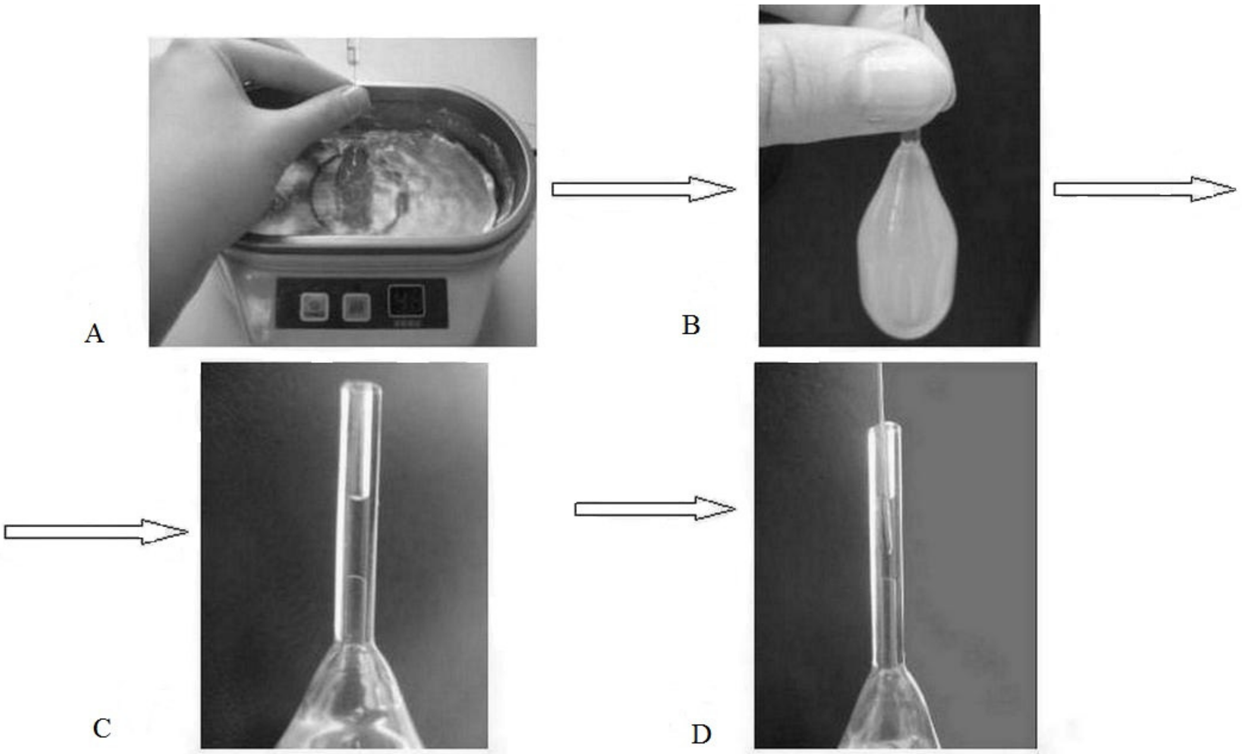

Figure 2
Scheme of preconcentration with ultrasonic dispersion of extractant

3 ml of the analyzed water was placed in the centrifuge tube. Then, using a microsyringe, 10 µL of extractant was introduced into the tube with simultaneous ultrasound exposure (Fig 2A). Exposure was carried out at 42 kHz, 60 W and (25±1)°C. According to [17] the ultrasound frequency of 42 kHz is the most suitable frequency range for emulsification. There is no undesirable chemical transformation of the extractant and impurities at this frequency. Irradiation was performed for 3 minutes. As a result, the emulsion of the organic solvent in the aqueous solution was formed (Fig 2B). Then centrifugation was performed for aggregation of the emulsion particles in the separate phase. In order to prevent evaporation of the extractant, the capillary centrifuge tube was capped with tubular polyethylene cover. Calculation of the volume of *n*-octane, which could evaporate and take the free part of the capillary above the surface of the extract, showed that it does not exceed 5.4×10^{-2} µL (as a liquid). This should not lead to the statistically significant error of determination. After centrifugation the extract was collected in capillary tube (Fig 2C). Then the aliquot was taken from the capillary into microsyringe (Fig 2D) and was injected into chromatograph. To calculate the initial concentration of the impurities in water, the extract was analyzed when the ratio of volume of initial water to volume of extractant was 1:1 since *R* in this case is 100 %. In this case water and extractant were placed in glass vial of 2 ml.

RESULTS AND DISCASSIONS

1. Extractant purification

Table 1 shows the purity of *n*-octane and ethanol before and after purification by Rayleigh distillation in ampoules with a mirror of evaporation 7.5 cm^2.

Table 1

The content of o-phthalates in solvents before and after purification by Rayleigh distillation (n=3, P=0.95)

Solvent	**Grade**	***o*-phthalate content, mg L^{-1}**				
		DMP	**DEP**	**DBP**	**DEHP**	**DNP**
n-Octane	TU 6-09-3748-74	$<1 \times 10^{-3}$	$<8 \times 10^{-4}$	$(3.0 \pm 0.6) \times 10^{-2}$	$(2.0 \pm 0.4) \times 10^{-2}$	$<1 \times 10^{-3}$
	purified	$<1 \times 10^{-3}$	$<8 \times 10^{-4}$	$<3 \times 10^{-3}$	$<3 \times 10^{-3}$	$<1 \times 10^{-3}$
Ethanol	GOST 1830087	$<1 \times 10^{-3}$	$(5.0 \pm 0.6) \times 10^{-1}$	$<3 \times 10^{-3}$	$<3 \times 10^{-3}$	$<1 \times 10^{-3}$
	purified	$<1 \times 10^{-3}$	$<8 \times 10^{-4}$	$<3 \times 10^{-3}$	$<3 \times 10^{-3}$	$<1 \times 10^{-3}$

It is seen from Table 1 that purification efficiency is high. After purification the impurity concentration was less than 4×10^{-4} mg L^{-1}. The rate of the evaporation was 6×10^{-4} g cm^{-2} s^{-1}. This enables us to purify 1 ml of the solvent during 4 minutes of evaporation. The purified *n*-octane was used as an extractant. The resulting volume of the purified solvent was sufficient for 90-95 extractions.

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2. Effect of irradiation time

Effect of time of ultrasonic irradiation on preconcentration has been investigated in the range from 20 sec to 10 min. Dependence of recovery on ultrasonic time impact is shown in Fig 3.

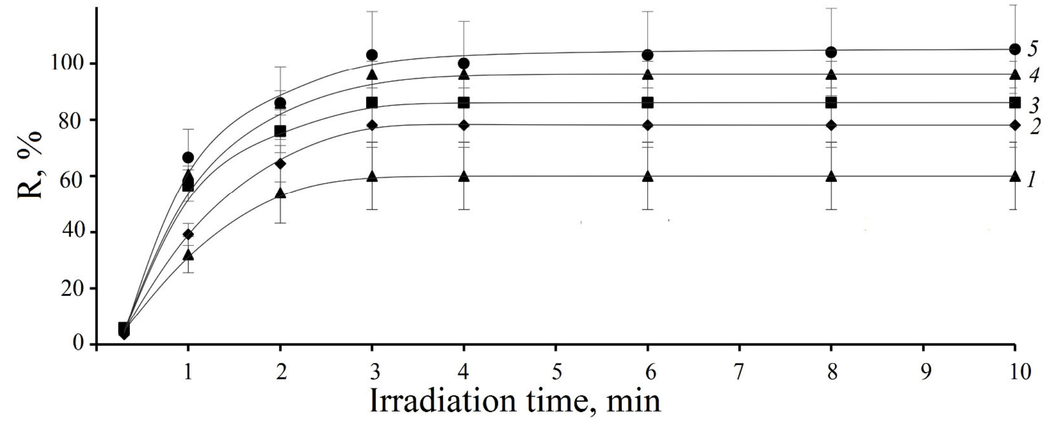


Figure 3

Effect of irradiation time on the recovery: 1 – DMP, 2 – DEP, 3 – DBP, 4 – DEHP, 5 – DNP.

As it can be seen, the increase of ultrasonic time impact led to the increase in the recovery of *o*-phthalates. The equilibrium value of recovery was achieved in about 3 minutes. These results are in agreement with literature data obtained for the determination of *o*-phthalates in bottled water [18].

3. Effect of centrifugation rate

As it follows from the monograph [19] the centrifuge separation factor is proportional to the square of the rotation frequency of the rotor:

$$F_r = \omega_{rt}^2 r_{rt} / g \, , \qquad (1)$$

Where F_r is the separation factor; ω_{rt} is the frequency of rotation; r_{rt} is the inner radius of rotation; g is the acceleration of free fall.

The effect of centrifugation speed on the preconcentration process was investigated in the range from 1000 to 7000 rpm at the time of centrifugation for 3 minutes. We have chosen the maximum possible frequency of rotation of centrifuge rotor at which there was no cracking of glass capillary branch. The study showed that at speed of more than 6000 rpm the centrifuge tubes were often cracked and thin glass capillaries were broken. For this reason the rate of 6000 has been chosen as the optimum one.

4. Effect of centrifugation time

Centrifugation time was changed from 1 to 10 min. As it can be seen from Fig 4, the extract volume did not statistically significantly change with the centrifugation time of more than 3 min. Thus, the time of 3 min was chosen as the optimum one.

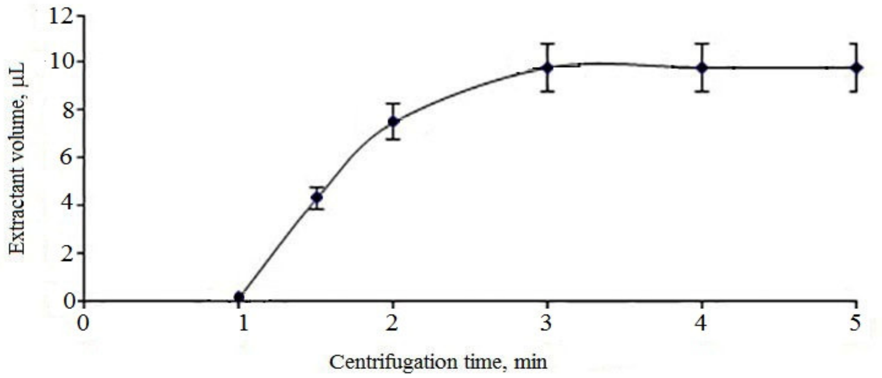


Figure 4
Effect of centrifugation time on the volume of the extract recovery

5. Effect of ionic strength

The effect of ionic strength on recovery has been investigated using tap water, bottled water and artificial mixtures prepared on the basis of double-distilled water. As it can be seen from Fig 5, the change in recovery is not statistically significant when the salt content in water samples is at the level of 2–2.5 % w/w or less. Starting from sodium chloride concentration of 2.5 % w/w and higher the recovery of all *o*-phthalates is reduced. The decrease in efficiency of preconcentration is probably due to the fact that the addition of salt impurities leads to the formation of hydrated ions of low mobility in solution which reduces the rate of diffusion of impurities determined in the organic extractant. Similar results have been obtained by the authors of other works [20, 21]. In further studies the salty additives were not used.

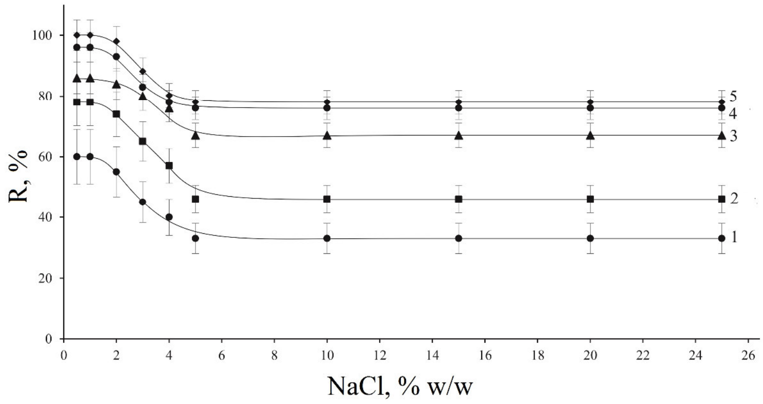


Figure 5
Effect of salt concentration on the recovery: 1– DMP, 2 – DEP, 3 – DBP, 4 – DEHP, 5 – DNP

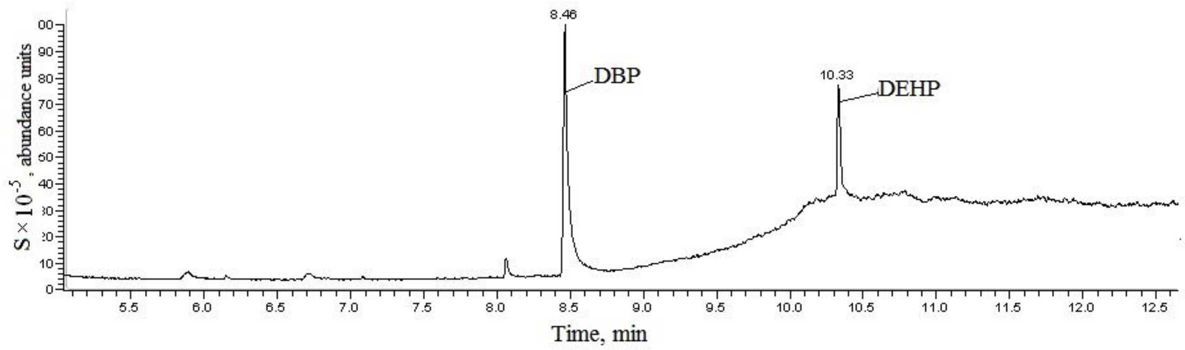
6. The material balance of the extractant in the extraction system

At this step the control of possible loss of the extractant by dissolving it in water and evaporation has been carried out. For this purpose the height of the extract column in the capillary after centrifugation was measured using a slide caliper and the volume of the separated extract was calculated. The height of the extract column was 6.43±0.05 mm. It corresponded to the volume of the extract of 9.90±0.27 µL. The initial volume of extractant introduced into the centrifuge tube was 10±0.1 µL. Comparison of these values shows statistically insignificance of extractant loss due to its dissolution and evaporation at microextraction. Experimental results are consistent with low solubility of *n*-octane in water and its low volatility.

7. Investigation of chromatographic septa

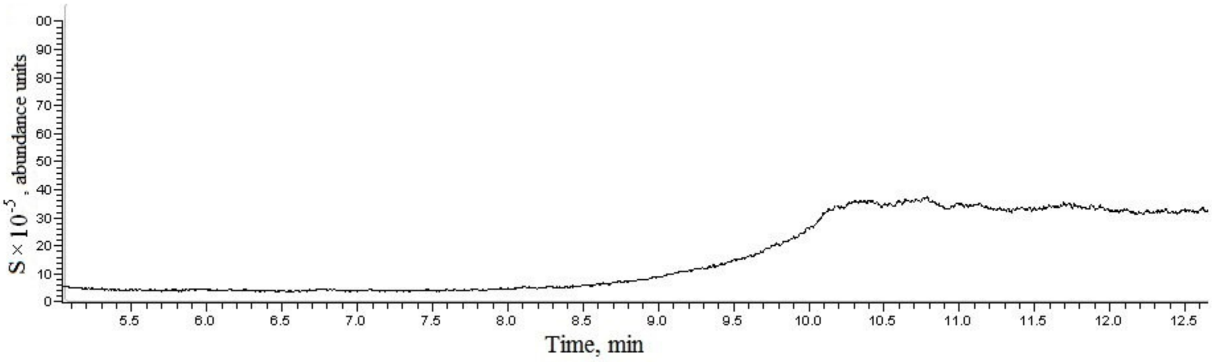
Leaching of *o*-phthalates from septum into carrier gas flow has been confirmed by gas-chromatography-mass-spectrometry analysis of high-purity *n*-octane. The results of analysis are shown in Fig 6A-C.

A



S – the area of chromatographic peak

B



C

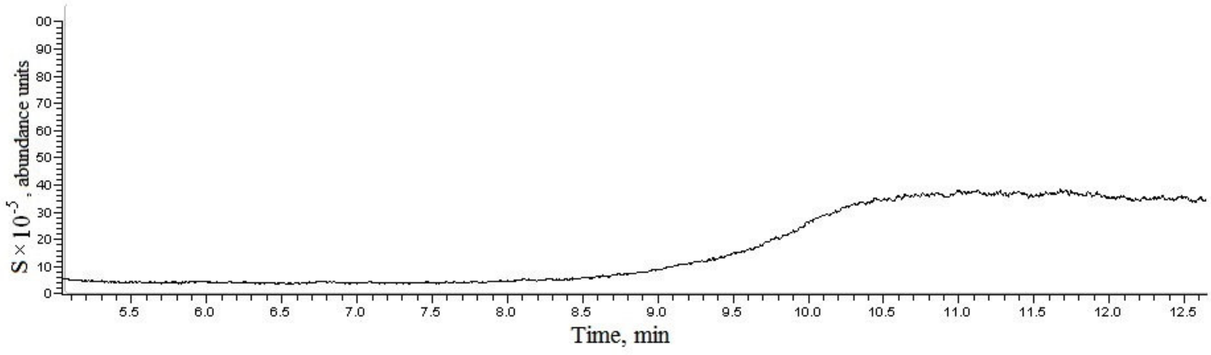


Figure 6

Figure 6A-C. A – chromatogram of n-octane, T_{inlet} = 280°C, septum Agilent P/N 5183-4757-S; B – Chromatogram of n-octane, T_{inlet} = 170°C, septum Agilent P/N 5183-4757-S; C – Chromatogram of n-octane, T_{inlet} = 280°C, septum Merlin.

It is seen from the chromatogram (Fig 6A) that the use of Agilent BTO septum (Bleed and Temperature Optimized) P/N 5183-4757-S leads to notable peaks of *o*-phthalates. They correspond to the absolute amount of each *o*-phthalate at the level of 10^{-7} mg. For other investigated septa (Agilent 5080-8894, Agilent 5183-4759-S, SGE AUTO-SEP Pkt.25 BATCH CO-01, Thermo-Finnigan 31303211, and Thermo-Finnigan 313 G 3211-1) the peak heights of *o*-phthalates were higher by 3–4 times more. The lowering of the injector port temperature down to 170°C completely eliminated the *o*-phthalates leaching (Fig 6B). The same results have been achieved with Merlin septum (Fig 6C). The Merlin septum contains a duckbill metal valve instead of plasticized polysiloxane septum (http://www.merlinic.com/products/merlin-microseal/how-the-merlin-microseal-works/). Based on these studies we used the Merlin septum during subsequent analyses.

8. Hydrolytic instability of o-phthalic acid esters

An important source of the formation of systematic errors in the determination of *o*-phthalates is related to their instability in aqueous solutions [22]. In an aqueous medium, the hydrolysis of *o*-phthalic acid occurs to result in the underestimated results of analysis. Thus, the hydrolysis of DEHP occurs according to the following reaction scheme:

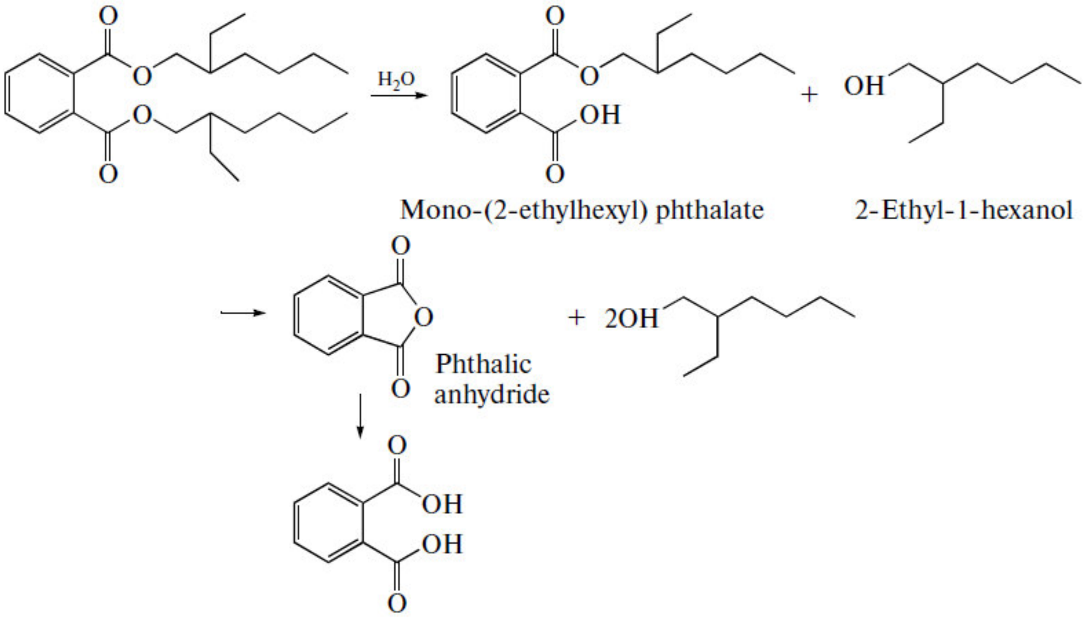


Figure 7
Illustrates the dynamics of hydrolysis of DMP, DEP, and DEHP

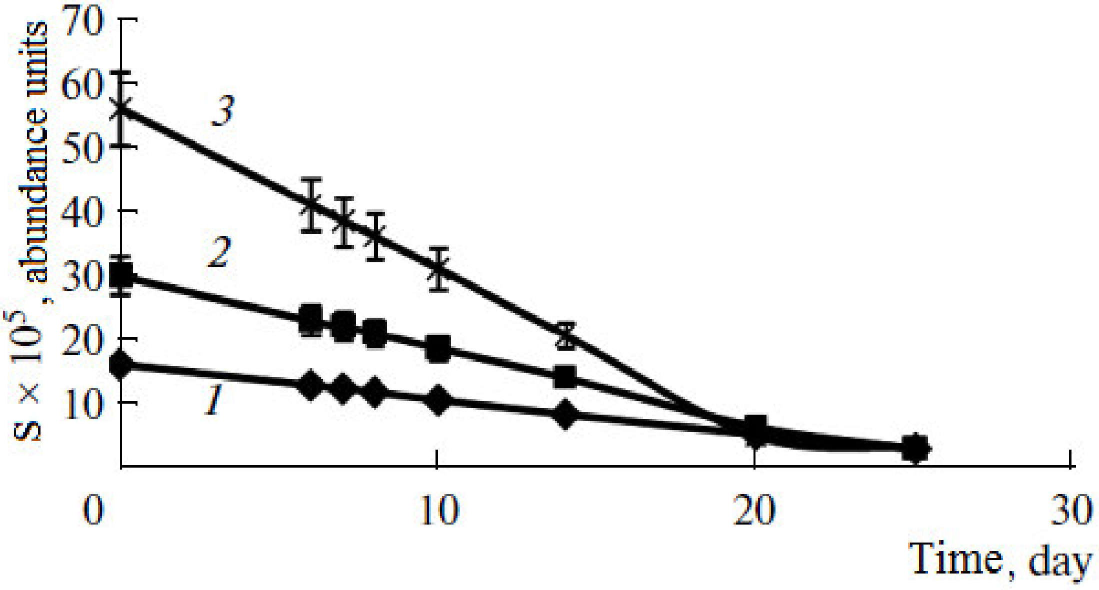


Figure 7
Dependence of the peak areas of (1) DMP, (2) DEP, and (3) DEHP on the storage time of aqueous solution at a temperature of (25 ± 1)°C.

It can be seen that *o*-phthalates of larger molecular weights are hydrolyzed more rapidly than low-molecular-weight ones. This may be related to the induction effect, which increases with the number of carbon atoms in the hydrocarbon radical. The published data [23, 24] also confirm the higher degree of hydrolysis of *o*-phthalates with larger molecular weights. Fig 7 also indicates that a statistically significant decrease in the concentration (no less than 20 %), which exceeds the random error in the determination of the most hydrolysable DEHP, was observed three days after the preparation of a model solution. After ten days, the concentration decreased by a factor of 1.6. Consequently, aqueous samples can be stored for no longer than three days after sampling.

9. Analytical performance of the proposed method

Recovery, enrichment factor, detection limit for macroextraction LOD and detection limit for microextraction LOD_{disp} are shown in Table 2.

Table 2

Recovery R, enrichment factors K, limit of detection LOD, limit of detection with dispergation LOD_{disp} of investigated impurities

Impurity	*R*, %	*K*	LOD, mg L^{-1}×10^5	LOD_{disp} , mg L^{-1}×10^5	MPC, mg L^{-1}×10^3 (1)
DMP	60 ± 3	180 ± 6	100	0.6	300
DEP	78 ± 6	230 ± 12	80	0.4	3000
DBP	86 ± 10	260 ± 25	300	1	200
DEHP	96 ± 10	290 ± 30	200	0.7	8
DNP	105 ± 10	315 ± 30	100	0.4	–

The limits of detection have been calculated based on the signal-to-blank standard deviation ratio of 3 [25, 26]. The blank standard deviation has been determined by analysis of pure *n*-octane contacted with the same volume of bidistilled water. The limits of detection for microextraction preconcentration (LOD_{disp}) have been found (The detection limits of microextraction preconcentration (LOD_{disp}) were calculated by dividing the detection limit of macroextraction preconcentration on the enrichment factor) using the enrichment factor. Linear range of determination of the target compounds was (0.02–30)×10^{-4} mg L^{-1}. As it seen from the Table 2, the detection limits, achieved with ultrasonic dispersion of extractant, are by several orders of magnitude lower than MPC. It makes it possible to establish the sources of pollution and to forecast the development of environmental situation long before attaining the critical one. Comparison of the results of this work and the results, obtained by the authors of other techniques for the determination of *o*-phthalates with LPME, is shown in Table 3. The table shows that the precision (RSD) of the determination is 3–7%. We have taken into account other factors that affect the reliability of the analysis and the expanded uncertainty of determination has been calculated. The relative combined standard uncertainty [30] of *o*-phthalates determination, and the contribution of the different constituents in the relative combined standard uncertainty are shown in Table 4. The relative expanded uncertainty has been calculated as follows

$$U = K\sqrt{U_1^2 + U_2^2 + U_3^2 + U_4^2 + U_5^2} \qquad (2)$$

It is at the level of 12–39 % (P=0.95, coverage factor K=2). The value of relative uncertainty increased with the decrease of the impurity concentration.

10. Real water samples analysis

The samples of tap, bidistilled and bottled water have been analyzed. The results of the analysis are shown in Table 5. *o*-Phthalates have been found at the level of 0.00002–0.002 mg L^{-1}. The presence of *o*-phthalates in water is confirmed by other studies [7, 9, 18, 29, 31]. As it can be seen from Table 5, DBP and DEHP were the most frequently detected *o*-phthalates.

11. Trueness control of the analysis results

Trueness confirmation is a very important part of the analysis [25-26]. In the present research the standard addition method has been used to confirm the trueness [32] of the proposed USAEME method. Real water sample – bottled still water, has been spiked with DBP and DEHP standards and has been analyzed by USAEME. Table 6 shows that the results of analysis are in a good agreement with the spiked amounts. The systematic error is statistically insignificant compared with the random one. This confirms the reliability of the achieved results.

Table 3
Comparison of the results of studies with LPME

Microextraction method	Extractant, µL	Water, ml	Analyte	Analytical method; injected volume, µl	Recovery, %; *(K)*	Precision (RSD),%	LOD$_{disp}$, mg L^{-1} ×10^{4}	Reference
Dynamic LPME	C_6H_{14}, 2	Tap, mineral, lake	DMP, DEP, DBP	GC-FID; 2	84-102; (28-95)	3.1-6.8	4.3-43	27
MLLME	CCl_4, 20	Waste-water, 10	DMP, DEP, DBP	HPLC-DAD; 20	82.7-116.9; (5-26)	1.2-10.5	12-22	28
DLLME	CCl_4, 41; dispersant – acetonitrile, 750	Tap, mineral, lake, 5	DMP, DEP, DBP	HPLC-DAD; 20	84-113; (44-196)	4.3-5.9	6.4-18	29
IL-CIA-DLLME	Ionic liquid, 32 µL; dispersant – acetonitrile, 750	Tap, bottled, mineral, river, 5	DMP, DEP, BBP	HPLC-DAD; 20	90.1-98.1; (174-212)	3.2-3.7	6.8-14	6
LDS-VSLLME	Toluene, 30	Bottled, 5	DMP, DEP, DBP, BBP, DEHP, DOP	GC-MS; 1	60-84; (200-290)	0.8-11.9	0.1^{-}80	7
AALLME	$C_2H_2Cl_4$, 15	Bottled mineral, 5	DMP, DEP, DiBP, DBP	GC-FID; 1	89-102; (910-1022)	2-4	1.2-11	8
USAEME	$CHCl_3$, 100	Bottled, tap, river, pool, sea 10	DMP, DEP, DBP, BBP, DEHP, DOP	GC-MS; 1	78-114; (78-114)	2-14	0.28-1.3	9
USAEME-SFO	1-undecanol, 30	Spring, tap, river, sea, 10	DMP, DEP, DAP, DiBP, DBP	HPLC-DAD; 30	107-123; (355-409)	8.7-12.6	0.05-0.1	10
USAEME	C_8H_{18}, 10	Tap, bidistillate, bottled, 3	DMP, DEP, DBP, DEHP, DNP	GC-MS; 10	60-105; (180-315)	3-7	0.04-0.1	This work

Abbreviations

LPME – liquid-phase microextraction; MLLME – membrane liquid-liquid microextraction; DLLME – dispersive liquid-liquid microextraction; IL-CIA-DLLME – ionic liquid cold-induced aggregation dispersive liquid-liquid microextraction; LDS-VSLLME – low-density solvent-based vortex-assisted surfactant-enhanced-emulsification liquid-liquid microextraction; AALLME – air assisted liquid-liquid microextraction; USAEME – ultrasound-assisted emulsification-microextraction; USAEME-SFO – ultrasound-assisted emulsification-microextraction with solidification of floating organic droplet; BBP – benzyl butyl phthalate; DOP – di-*n*-octyl phthalate; DiBP – diisobutyl phthalate; DAP – diallyl phthalate; DiHP – diisoheptyl phthalate; RSD – relative standard deviation

Table 4
The contribution of various factors to the combined standard uncertainty

Source of uncertainty Type of uncertainty	Precision, U_1	Preparation of the standards, U_2	Calibration curve, U_3	Sample introduction, U_4	Enrichment factor, U_5
Relative standard uncertainty, %	3-7	3–8	0.3–8	0.6	4–14
Relative combined standard uncertainty, %			5.9–19.4		

Table 5
Results of water analysis, (n=3, P=0.95)

Water sample	Impurity content, mg L^{-1}×10^{3}				
	DMP	DEP	DBP	DEHP	DNP
Tap [a]	$<6 \times 10^{-3}$	$<4 \times 10^{-3}$	$<1 \times 10^{-2}$	$<7 \times 10^{-3}$	$<4 \times 10^{-3}$
Bidistillate [a]	$<6 \times 10^{-3}$	$<4 \times 10^{-3}$	$<1 \times 10^{-2}$	$<7 \times 10^{-3}$	$<4 \times 10^{-3}$
"Svyatoy istochnik"(Russia) [a, g]	$<6 \times 10^{-3}$	$<4 \times 10^{-3}$	$<1 \times 10^{-2}$	$<7 \cdot 10^{-3}$	$<4 \times 10^{-3}$
"Sarova"(Russia) [a, g]	$<6 \times 10^{-3}$	$<4 \times 10^{-3}$	$<1 \times 10^{-2}$	$<7 \times 10^{-3}$	$<4 \times 10^{-3}$
"Ya"(Russia) [a, g]	$<6 \times 10^{-3}$	$<4 \times 10^{-3}$	$<1 \times 10^{-2}$	$<7 \times 10^{-3}$	$<4 \times 10^{-3}$
"Shishkin Les"(Russia) [a, g]	$<6 \times 10^{-3}$	$<4 \times 10^{-3}$	0.08 ± 0.02	2.1 ± 0.5	$<4 \times 10^{-3}$
"Arkhyz"(Russia) [a, g]	$<6 \times 10^{-3}$	$<4 \times 10^{-3}$	0.4 ± 0.1	1.8 ± 0.4	$<4 \times 10^{-3}$
"VALON"(Germany) [a, g]	$<6 \times 10^{-3}$	$<4 \times 10^{-3}$	0.10 ± 0.02	1.5 ± 0.3	$<4 \times 10^{-3}$
"Re:newal premium spring water"(USA) [a, g]	$<6 \times 10^{-3}$	$<4 \times 10^{-3}$	$<1 \times 10^{-2}$	$<7 \times 10^{-3}$	$<4 \times 10^{-3}$
"Aquador" (Denmark) [a, g]	$<6 \times 10^{-3}$	$<4 \times 10^{-3}$	$<1 \times 10^{-2}$	$<7 \times 10^{-3}$	$<4 \times 10^{-3}$
"Novelle" (Finland) [a, g]	$<6 \times 10^{-3}$	$<4 \times 10^{-3}$	$<1 \times 10^{-2}$	$<7 \times 10^{-3}$	$<4 \times 10^{-3}$
Bottled[b]	$<2 \times 10^{-2}$	$<4 \times 10^{-3}$	$<1 \times 10^{-2}$	$<7 \times 10^{-3}$	$<4 \times 10^{-3}$
Bottled[c]	5.1×10^{-2}	3.2×10^{-1}	4×10^{-1}	2.5×10^{-1}	1.2×10^{-1}
Drinking [d, g]	–	2.5×10^{-1}	–	–	–
Mineral[e]	–	–	11.3	–	9.1
Mineral [f, g]	–	3.2	5.4	–	–

[a] This work, [b](7), [c] (9), [d](18), [e](29), [f](31), [g] bottled still water

Table 6
Confirmation of the trueness determinations of analytes by standard addition method, (P=0.95; n=4), mg $L^{-1}\times 10^3$

Analyte	Sample	Added	Found
DBP	0.4 ± 0.1	0.3	0.8 ± 0.2
DEHP	1.8 ± 0.4	1.2	2.9 ± 0.5

Possible sources of *o*-phthalate esters in bottled water are plasticized gaskets for bottle caps. Our investigations with the use of carbon tetrachloride as an extractant for extraction of *o*-phthalates from gaskets of plastic bottles have shown the composition of gaskets contains at least 20 % of DEHP and DBP [33]. This is also confirmed by the patent documents and the other literature [34-36] according to which the gaskets of the bottle caps are made of polymers, PVC, PVA, polystyrene, polycarbonate, polyester, etc., plasticized by esters of *o*-phthalic acid.

CONCLUSION

This study shows that the ultrasound-assisted emulsification-microextraction is an efficient method for preconcentration of *o*-phthalates, it allows to carry out analysis of real water samples. The process takes not more than 6 minutes, and the recoveries of impurities reach the value of 60–105%. Application of extract capillary collection solves the problem of sampling of “light” extract and eliminates the loss of the extract connected with evaporation. To eliminate the *o*-phthalates leaching into the carrier gas flow from the plasticized chromatographic septum, the Merlin septum was used. For purification of solvents the Rayleigh distillation was used. The relative expanded uncertainty of *o*-phthalates determination is at the level of 12–39 %. Achieved gas-chromatographic-mass-spectrometric limits of *o*-phthalates detection are at a level of 4×10^{-6}–1×10^{-5} mg L^{-1} and not inferior to the best obtained results.

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