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Vapour-phase extraction for the isolation of organic compounds from aqueous solutions

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Method of vapour-phase extraction is offered for the isolation of organic compounds from aqueous solutions, the mechanism of the phenomenon is considered.

Liquid and gas extractions, steam distillation and adsorption are currently used for the isolation of organic compounds from water. Steam distillation can be effective only for volatile substances,[1] and it has significant difficulties if target substances are hydrophilic.[2] The theoretical bases of liquid extraction allow one to predict the efficiency of extractive systems. At the same time, the partition coefficient ($K = c_{\mathrm{organic}}/c_{\mathrm{water}}$) of well-soluble organic compounds does not exceed 50 even in the most successful solvent–water system.[3] The use of hydrophobic alcohols (amyl–decyl) and acetic acid esters (butyl–heptyl) as extractants has shown that the extractive activity regularly raises with decreasing number of carbon atoms in the solvents molecules-homologues. However, its water solubility grows, that does not allow one to apply low molecular weight homologues without a salting-out procedure.[4]

In this work, we used hydrophilic organic liquids for the isolation of soluble organic substances from aqueous solutions. This is vapour-phase extraction (VPE), extraction by the vapour of an organic extractant. Aqueous solutions of low-molecular-weight carboxylic acids and phenols were the test materials.

For the VPE of dissolved organic substances from water, we used a device,[5,6] which is schematically shown in Figure 1.

The extractant used for VPE should have a boiling point lower than the boiling temperature of the test sample. The sample is heated up to the boiling point for evaporating an added extractant. For the isolation of unstable substances, the VPE temperature can be lowered by lowering pressure with a vacuum pump through branch tube *7*. At VPE under positive pressure conditions the vacuum pump changes for a compressor.

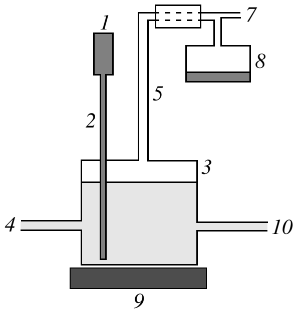

Figure 1 Device for the vapour-phase extraction of organic compounds (VPE module): (*1*) liquid pump for giving extractant; (*2*) pipeline; (*3*) distilling vessel with the initial liquid sample; (*4*) pipeline for giving the sample; (*5*) vapour pipeline; (*6*) condenser; (*7*) branch tube for connecting the compressor or vacuum pump; (*8*) receiver for VPE condensate; (*9*) heater; (*10*) exit pipe.

It is possible to carry out VPE in a static mode. In this case, a hydrophilic organic liquid or insoluble extractant with a density greater than that of the sample is given by pump *1* into the volume of sample *3*. The extraction can be batch and multiple-batch, when before the next addition of the following extractant portion (same or another) the sample is cooled below the extractant boiling temperature. A series of sequential VPE extracts enables us to increase the degree of extraction.

VPE in a dynamic mode provides continuous giving liquid extractant by pump *1* in volume of specimen previously heated up to extractant boiling point and then supported by a heater *9*. In this mode, it is also possible to continuously give the initial sample.

It is established that the extraction degree depends on the individual characteristics of dissolved organic compounds and the type of extractant. For an explanation of the obtained results, the theoretical model is offered. It considers the investigated phenomenon as the distribution of a target compound between two phases: liquid (water) and vapour of added organic extractant.

Gas extraction is widely used in chemical analysis. A target component is moved on gas medium (nitrogen, argon *etc.*), contacting with a liquid.[7] However, gas extraction has essential differences from VPE, where the isolation of compounds is made into the vapour of an organic extractant. In our researches, the critical temperatures of used extractants are much higher than the temperatures of investigations. In view of the usual terminology and standard classification, it allows us to call extraction of target components from water by vapour of organic liquid a vapour-phase extraction.

The proof of the participation of a solvent vapour in the isolation of organic compounds from water is given in Table 1. In case of ethanol addition to the aqueous solution of a mix of organic acids and heat, the increase of its equilibrium concentrations in a vapour-gaseous phase in comparison with gas extraction (without alcohol) is observed. Collecting and con-

Table 1 The results of analysis of a vapour-gas phase at 100 °C above an aqueous solution of carboxylic acids with and without the additition of spirit to the sample.[a]

Experiment	Concentration of organic acids in a vapour-gas phase/μg cm^{-3}				
	C_2	C_3	C_4	C_5	C_6
VPE (3% EtOH)	0.23±0.012	0.65±0.063	0.68±0.090	0.96±0.073	1.20±0.11
GE	0.14±0.035	0.30±0.028	0.38±0.034	0.52±0.060	0.64±0.068

[a] The concentrations of organic acids in both experiments were as follows (μg cm^{-3}): acetic (C_2), 324; propionic (C_3), 368; butyric (C_4), 287; pentanoic (C_5), 304; hexanoic (C_6), 305.

Table 2 Three-multiple vapour-phase alcohol extraction of C_2–C_4 acids from water (pH 3–4).[a]

V_{org}/V_{water}	n	no.	V_D/cm^3	C_{EtOH} (vol%) after VPE		$^*K_{eq}$		
				condensate	sample	acetic acid	propionic acid	butyric acid
1:30	11	1	15±2.3	39±2.3	1.2±0.21	0.32±0.036	1.1±0.13	2.1±0.20
	10	2	16±1.2	49±2.6	1.8±0.24	0.36±0.045	1.0±0.10	1.8±0.21
	10	3	17±1.4	52±2.5	2.0±0.44	0.27±0.038	0.9±0.10	1.8±0.22
2:30	3	1	36±5.8	40±6.8	1.7±0.65	0.31±0.095	0.7±0.30	1.3±0.52
	3	2	32±1.1	50±3.6	2.0±1.2	0.20±0.10	0.6±0.32	1.0±0.62
	3	3	35±1.1	53±2.2	3.0±2.2	0.18±0.090	0.5±0.33	1.1±0.66
3:30	3	1	44±6.0	52±1.8	2.2±0.68	0.25±0.046	0.7±0.16	1.1±0.18
	3	2	48±4.9	58±5.1	3.2±0.78	0.22±0.064	0.6±0.11	1.08±0.053
	3	3	49±6.8	63±4.8	4.0±1.8	0.21±0.053	0.64±0.035	1.1±0.20

[a] V_{org}/V_{water} is the ratio of volumes of spirit and water solution of organic acids before VPE; n is the number of replicate analyses; no. is the serial number of a VPE extract; V_D is the volume of a condensate (VPE extract); C_{EtOH} is the spirit concentration; $^*K_{eq}$ is the VPE factor. Initial concentrations of C_2, C_3 and C_4 were 50–170, 50–150 and 35–180 μg cm^{-3}, respectively.

Table 3 Three-multiple vapour-phase extraction of C_2–C_4 acids from water by different extractants (pH 3–4, V_{org}/V_{water} = 1:30).[a]

Extractant	n	no.	V_D/cm^3	$C_{extractant}$ (vol%) after VPE		$^*K_{eq}$		
				condensate	sample	acetic acid	propionic acid	butyric acid
MeOH	4	1	16.2±0.54	28±2.4	1.9±0.13	0.5±0.12	1.7±0.40	3.1±0.57
	4	2	16±2.7	37±4.0	3.33±0.068	0.38±0.053	1.2±0.12	2.3±0.22
	4	3	16±1.5	39±9.9	4.7±0.59	0.32±0.060	1.1±0.27	2.1±0.55
Pr^{i}OH	3	1	14±1.5	49±8.7	0.8±0.22	0.38±0.078	1.30±0.088	2.5±0.13
	3	2	16±2.5	50±10.8	1.0±0.35	0.32±0.080	1.21±0.077	2.4±0.19
	3	3	16±1.9	57±7.0	1.2±0.41	0.33±0.064	1.1±0.14	2.2±0.49
CCl_4	3	1	10±1.1	97±2.8	0.3±0.22	0.005±0.0014	0.013±0.0032	0.06±0.009

[a] See footnote to Table 2.

densing the vapour of an added solvent in a separate vessel at evaporation from sample, we produced an extract condensate containing target compounds.

From our point of view, the mechanism of VPE is the following: at evaporating the added organic solvent (spirit) from the water solution it is isolated in an individual vapour phase in the volume of a sample (bubble) and above the solution surface in the distilling vessel. The liquid–vapour heterogeneous system is formed. The molecules of the dissolved compounds continuously pass from one phase into another and back. The solvent vapour is the extractant in relation to water.

The rates of compound migration from one phase into another are proportional to the corresponding concentrations of extractable substances. For the rate of molecular transition from a liquid phase υ_L into vapour and back υ_V, there are the following equations:

$$\upsilon_L = k_L c_L, \tag{1}$$

$$\upsilon_V = k_V c_V, \tag{2}$$

k_L, k_V are the rate constants; c_L is the concentration of an extractable compound in the liquid phase; c_V is its concentration in vapour.

Under the conditions of dynamic equilibrium:

$$\upsilon_L = \upsilon_V, \tag{3}$$

$$k_L c_L = k_V c_V, \tag{4}$$

$$c_V/c_L = k_L/k_V = K_{eq}. \tag{5}$$

The assumption about a dynamic equilibrium of transition of volatile organic substances in the vapour from solution and back is based on the following. It is well known,[7] that the distribution equilibrium of volatile substances between a liquid and a gas at gas extraction is achieved at a gas flow rate up to 0.5 dm^3 min^{-1}. Even in the dynamic mode of VPE, the speed of formation of alcohol vapour in the aqueous solution at the speed of giving an alcohol at 1 cm^3 min^{-1} is equal to 22.4×1×0.8/46 ≈ ≈ 0.4 dm^3 min^{-1}, where 22.4 dm^3 min^{-1} is the molar volume; 46 g mol^{-1} is the alcohol mole; 0.8 g cm^{-3} is the density of the alcohol. Thus, the rate of formation of alcohol vapour in the specimen volume under these conditions corresponds to an equilibrium mode of gas extraction.

Taking into account a material balance, when in the beginning the target compound is completely concentrated in water, it is possible to write

$$m_0 = m_L + m_V, \tag{6}$$

where m_0 is the initial mass of the compound in a liquid specimen (water); m_L is its mass in the liquid phase at equilibrium; m_V is its mass in a vapour phase at equilibrium.

Considering (6), equation (5) can be rewritten as:

$$K_{eq} = (m_0 - m_L)V_L/m_L V_V = (m_0/m_L - 1)V_L/V_V, \tag{7}$$

where V_L is the liquid volume; V_V is the vapour volume.

At VPE, all vapour is condensed and collected in receiver *8* (Figure 1). The mass of the formed vapour M_V is equal to the mass of the produced condensate M_D:

$$M_V = M_D, \tag{8}$$

$$V_V \rho_V = V_D \rho_D, \tag{9}$$

$$V_V = (\rho_D/\rho_V)V_D, \tag{10}$$

where ρ_D is the density of the produced condensate; ρ_V is the density of a vapour phase, V_D is the condensate volume.

From (8)–(10), it is possible to write:

$$^*K_{eq} = K_{eq}(\rho_D/\rho_V) = V_L/(m_0/m_D - 1)V_D, \tag{11}$$

where m_D is the mass of the extractable compound in the condensate, $m_D = m_V$.

In VPE, the densities of a vapour phase ρ_V and a condensate ρ_D depend on the concentration of water, the extractant and volatile organic substances. Thus, the ratio ρ_D/ρ_V in equation (10) remains constant because, at every moment, the vapour and condensate received from it have identical compositions. Therefore, it is incorporated with K_{eq}. Equation (11) is the integrated characteristic of VPE because during the extraction fluctuation of composition and density both vapour and collected condensate are probable. Nevertheless, as experimental data indicate (Table 2), equation (11) is valid. The calculated factor $^*K_{eq}$ as the equilibrium constant should not depend on component concentrations or the volumes of water samples and extractants. Its small decrease during three-multiple sequential vapour-phase alcohol

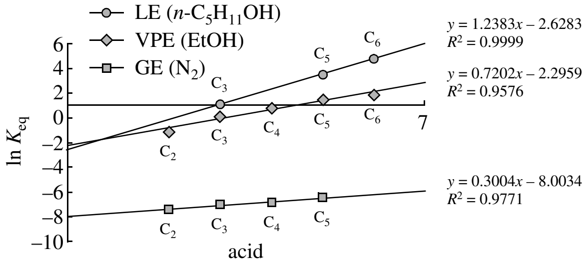

Figure 2 Dependence of the logarithm of extractive factor on the amount of carbon atoms in the acid molecule in liquid (LE), vapour-phase (VPE) and gas extraction (GE) from water.

extraction of C_2–C_4 acids with increasing volume of the extractant is connected with the growth of the concentration of spirit, remaining in the specimen after VPE.

The $^*K_{eq}$ is a function of physical and chemical properties of an isolable compound and extractant. It was obtained, that the replacement of spirit with methanol (Tables 2 and 3) resulted in an appreciable increase. Isopropyl alcohol was approximately identical with ethanol activity in VPE. At a choice for VPE of those aliphatic acids hydrophobic organic solvent carbon tetrachloride there is a large decrease of VPE factor. The factor $^*K_{eq}$ for butyric acid in this case decreases more than 30 times.

The VPE in a dynamic mode uses continuously giving extractant by pump *1* (Figure 1) in the volume of the previously heated up sample to extractant boiling point. The results of determination of $^*K_{eq}$ for low-molecular-weight carboxylic acids by ethanol from water with various speed of giving spirit are submitted in Table 4. In experiment through some interval of time (time extraction), not stopping process, the assembled portion of extract-condensate was analysed by gas chromatography. As follows from the experiment (Tables 2 and 4), extractive equilibrium in the vapour–liquid system, which was supposed at theoretical consideration of the VPE mechanism, already has time to exist in the range of speeds of giving extractant of 1–2 cm^3 min^{-1}.

Table 4 Vapour-phase alcohol extraction of low-molecular-weight acids from water in a dynamic mode (pH 3–4).

Extractable compound	$^*K_{eq}$			
	EtOH supply rate, 1 cm^3 min^{-1}		EtOH supply rate, 2 cm^3 min^{-1}	
	VPE duration/min	$^*K_{eq}$	VPE duration/min	$^*K_{eq}$
Acetic acid	25	0.35±0.031	20	0.37±0.033
	20	0.36±0.039	20	0.22±0.020
			20	0.18±0.024
			20	0.18±0.022
			20	0.17±0.022
			20	0.19±0.026
Propionic acid	25	0.69±0.067	20	0.82±0.089
	20	0.71±0.079	20	0.53±0.063
			20	0.46±0.063
			20	0.45±0.069
			20	0.44±0.062
			20	0.42±0.055
Butyric acid	25	1.36±0.098	20	1.40±0.16
	20	1.40±0.11	20	0.81±0.084
			20	0.72±0.086
			20	0.67±0.072
			20	0.69±0.077
			20	0.68±0.075

Table 5 Isolation of organic compounds from water by gas, vapour-phase and liquid extraction.

Extractable compound	Extraction factor $K_{eq} = C_{org}/C_{water}$				
	GE[7]	VPE $^*K_{eq} = K_{eq}(\rho_D/\rho_V)$		LE[3]	
	N_2	MeOH	EtOH	n-$C_5H_{11}OH$	Et_2O
Acetic acid	0.00059	0.5±0.12	0.34±0.037	—	0.5
Propionic acid	0.00089	1.7±0.40	1.1±0.13	2.98	1.86
Butyric acid	0.00105	3.1±0.57	2.1±0.20	—	6.31
Pentanoic acid	0.00152	4.4±0.55	4.2±0.43	34.7	10.0
Hexanoic acid	—	6.4±0.58	6.0±0.54	123.0	93.3
Phenol	0.000101	—	0.61±0.075	36.8	17.0
m-Cresol	0.000137	—	0.97±0.087	—	—
p-Cresol	0.00013	—	0.94±0.081	192	—
o-Cresol	0.0003	—	2.2±0.024	92.5	—

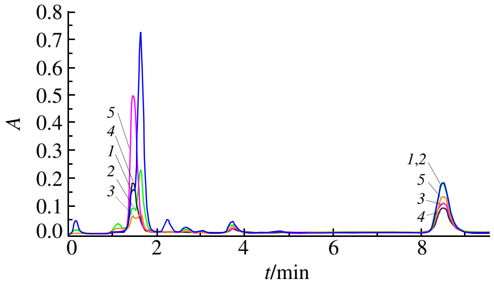

Figure 3 HPLC chromatogram of a VPE (acetonitrile) extract of hydrogen sulfide underground water: column C_{18}(5 μm) 80×2 mm, eluent (acetonitrile–water, 9:1), 100 μl min^{-1}; wavelengths, (*1*) 220, (*2*) 230, (*3*) 240, (*4*) 250 and (*5*) 270 nm.

Thus, in contrast to traditional liquid extraction, the VPE method enables us to use hydrophilic organic liquids as extractants.

In comparison with gas extraction, at VPE, choosing from a number of hydrophilic or hydrophobic organic solvents, it is possible to:

i. selectively extract classes or groups of organic compounds;

ii. achieve selective isolation of individual compounds by the applying various extractants in multiple-bath VPE.

In Table 5, for comparison, the extractive factors of C_2–C_6 organic acids and phenols are submitted at their gas, vapour-phase and liquid extractions from water. It can be seen that the VPE method occupies an intermediate place on extractive efficiency of those organic compounds from a water medium.

The unique capabilities of VPE are illustrated by the analysis of natural organic matter in mineral waters. Using VPE in combination with HPLC-UV, we found natural sulfur organic compounds in sulfide underground waters of the field Matsesta (Sochi, Russia). HPLC chromatograms of a VPE extract of hydrogen sulfide underground water at wavelengths from 220 to 270 nm are presented in Figure 3. At present, the chemical structure of the discovered substances is not established. Preliminary mass-spectrometric analysis has shown the presence of the carbon–sulfur fragments –C–S– (or –C=S) and –C–S–C– in their molecules.

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