Micro Liquid-Liquid Extraction of Acetyl Derivatives of Phenols

by Andrzej Urbanczyk[1], Jacek Staniewski[1], Wieslaw Apostoluk[2] and Jan Szymanowski[1*]

[1] Institute of Chemical Technology and Engineering, Poznan University of Technology, pl. M. Sklodowska-Curie 2, 60–965 Poznań, Poland
[2] Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wroclaw, Wybrzeże Wyspiańskiego 27, 50–370 Wrocław, Poland

Micro liquid-liquid extraction of phenols acetyl derivatives from aqueous solution was studied and distribution coefficient was successfully correlated with solvent and solute property parameters. Toluene selected as a solvent for the extraction proved to be appropriate for the process. Extraction depended mainly on the hydrophobicity of phenol acetyl derivatives and the ionic strength of the aqueous solution. With the use of large volume on-column sample introduction technique it was possible to determine phenols at the level of 1 µg L^{-1} both in model and environmental samples with a flame ionization detector.

Zastosowano metodę mikroekstrakcję ciecz-ciecz do wydzielania fenoli z próbek wodnych. Fenole ekstrahowano w postaci pochodnych acetylowych, przeprowadzając derywatyzację bezpośrednio w próbce wodnej za pomocą bezwodnika kwasu octowego. Wyznaczono współczynniki podziału acetylowych pochodnych fenoli pomiędzy fazę wodną i organiczną, które z powodzeniem skorelowano z parametrami rozpuszczalników oraz badanych związków. Odpowiednim ekstrahentem do tego celu okazał się toluen. Ekstrakcja zależała głównie od hydrofobowości acetylowych pochodnych fenoli oraz siły jonowej roztworu wodnego. Dozowanie próbki o dużej objętości metodą on-column pozwoliło na oznaczanie fenoli na poziomie 1 µg L^{-1}, zarówno w przypadku modelowych próbek wodnych, jak i próbek środowiskowych, przy zastosowaniu detektora płomieniowo-jonizacyjnego.

* Corresponding author. E mail: Jan.Szymanowski@put.poznan.pl

Phenols are commonly encountered in aqueous effluents arising in a variety of manufacturing processes. Solvent extraction with various organic solvents is a classical method used for separation of phenols from various technological solutions [1,2].

Phenols, and particularly chlorinated phenols are toxic pollutants, frequently found in surface and tap waters. Capillary gas chromatography is often used to its determination at trace levels [3–8]. However, sensitive and selective detectors such as mass spectrometry with single ion monitoring (MS–SIM), mass selective detector (MSD) or electron capture detector (ECD) for chlorinated phenols had to be used. Preconcentration and large volume sample introduction (LVI) is needed when non-selective or less selective detectors, *i.e.* flame ionization detector (FID) is used [9–15].

Micro liquid-liquid extraction (μLLE) combined with gas chromatography can be successfully applied [16–20]. However, phenols are weak acids and can dissociate in aqueous solutions, even at pH near 7 when they contain electron withdrawing substituents, *e.g.* nitro groups. As a result, the acidity of the aqueous solution must be strictly controlled because anionic species of phenols are not extracted by organic solvents.

This problem can be eliminated in industrial processes by the use of various basic or solvating hydrophobic reagents, *e.g.* alkyl amines, tributhyl phosphate, trialkylphosphine oxides *etc.* dissolved in an organic solvent [21]. Analyzing phenols, it is very convenient to convert them into appropriate derivatives, especially acetyl derivatives. Acetic anhydride can be used and the acetylation reaction can be carried out *in situ* in the water sample, just before the extraction step [5–8,17,20]. As a result, we can expect a better extraction because as phenol acetyl derivatives are less hydrophilic than phenols, the extraction is less sensitive to pH and a better resolution is achieved in gas chromatographic determination.

The aim of this work was to study the recovery of phenol acetyl derivatives using μLLE.

EXPERIMENTAL

Materials

The following phenols were used: phenol, pure for analysis, from POCh (Poland); 4-methylphenol, 98% purity, from Merck (Germany); 3-chlorophenol, 98%; 2,3-dimethylphenol, 98%; 4-chloro-3-methylphenol, 99%; 2,4-dichlorophenol, 99%; 2,4,6-trichlorophenol, 98%; each from Sigma–Aldrich (Germany). A stock solution of each phenols was prepared in acetonitrile, from Fluka AG (Germany). It contained 1800–2000 ng μL^{-1} of a phenol. Acetic anhydride, pure for analysis, from POCh (Poland) was used for derivatization of phenols. Potassium carbonate, pure for analysis, from POCh (Poland) was used to achieve basic solution. Hexane, 95%, from J.T. Baker (Holland), dichloromethane, 99.9% (HPLC grade), from Sigma–Aldrich (Germany) and toluene, pure for analysis, from POCh (Poland) were used in extraction experiments. Hexane and toluene were distilled prior its use. Decane from Merck (Germany) was used as an internal stan-

dard to determine extraction efficiency. The solution in hexane contained about 1000 ng μL^{-1} of the mentioned hydrocarbon.

Derivatization and extraction procedure

Phenols were extracted from water samples as their acetyl derivatives. Acetic anhydride was used as derivatizating agent. Derivatization was carried out directly in water sample in a separatory funnel as detailed in the scheme given in Figure 1.

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┌─────────────────────┐    ┌─────────────────────┐    ┌─────────────────────┐
│  Water sample spiked│    │ Alkalisation of     │    │     Acetylation     │
│  with phenols       │ => │ sample              │ => │  0.5 ml acetic      │
│  (100 ml)           │    │ 1 g K₂CO₃ (pH~11)   │    │  anhydride          │
└─────────────────────┘    └─────────────────────┘    └─────────────────────┘
                                                                  ⇓
                                                       ┌─────────────────────┐
                                                       │    Salting-out      │
                                                       │      (NaCl)         │
                                                       └─────────────────────┘
                                                                  ⇓
┌─────────────┐    ┌─────────────────────┐    ┌─────────────────────┐
│ GC analysis │ <= │  Extract drying     │ <= │ Extraction with     │
│             │    │  (Na₂SO₄)           │    │ organic solvent     │
└─────────────┘    └─────────────────────┘    └─────────────────────┘
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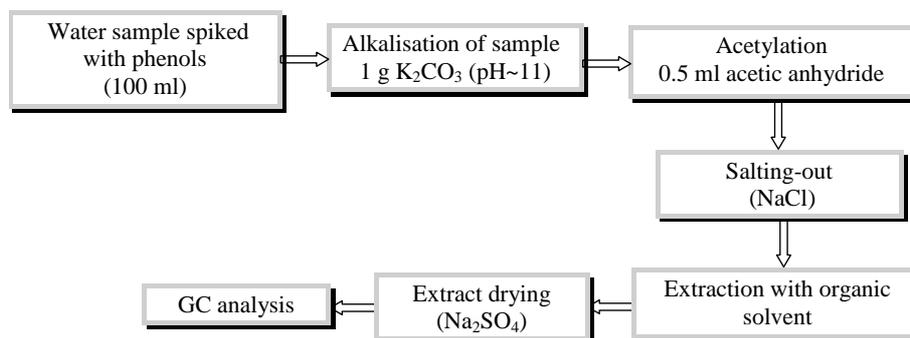
Figure 1. Analytical scheme

The tap water sample (or river water) was spiked with phenol mixture to achieve concentration 4 μg L^{-1}. After the dissolution of potassium carbonate and addition of acetic anhydride, the separatory funnel was shaken vigorously by hand for 5 min and then left for next 5 min. This gave a solution with a final pH about 8. After derivatization sample was saturated with various amounts of sodium chloride. Each extraction was accomplished by shaking with organic solvent spiked with the internal standard for 5 min and allowing the layers to separate completely. Obtained extract was dried over anhydrous sodium sulfate. The extraction was repeated twice. Chromatographic analysis was performed after each stage of extraction.

Extraction efficiency (%E) was calculated as follows:

$$\%E = \frac{S_F^1 / S_W^1}{\sum_{i=1}^{n} S_F^i / S_W^i} \tag{1}$$

where: S denotes the area of corresponding peaks, subscripts F and W denote the considered compound and the standard (decane), superscripts 1 and i denote the number of extraction stage.

The distribution coefficient was determined according to the following equation:

$$D = \frac{V_w / V_o \times \%E}{100 - \%E} \tag{2}$$

where: V denotes the volume of water (subscript w) and organic (subscript o) phase.

Equipment and GC parameters

GC analyses were performed with Carlo Erba HRGC 5300 Mega Series instrument, equipped with home-made large volume on-column injection system, flame ionisation detector (FID), solvent vapour exit (SVE), pressure regulation system and PC-based data system Chromeleon (Gynkotek) to control data acquisition. The following precolumn system was placed in a GC oven: 10 m × 0.53 mm deactivated fused-silica capillary column (retention gap) with 3 m × 0.32 mm × 0.25 μm CP–Sil 8 CB (Chrompack) capillary column (retaining precolumn) connected using a press-fit connector. The analytical column was 27 m × 0.32 mm × 0.25 μm CP–Sil 8 CB (Chrompack) capillary column. The solvent vapour exit was placed between the retaining precolumn and the analytical column. Carrier gas was helium (99.999% purity), inlet pressure was 100 kPa. The pressure of helium was controlled by a pressure regulation system, consisting of a pressure regulator, back-pressure regulator and mass flow controler. Analysis were carried out in the following temperature programmed conditions: initial oven temperature was held at 40°C for 3 min, then at 5°C min^{-1} to 220°C, followed by 10°C min^{-1} to 280°C min^{-1} and, finally, held for 10 min. Detector temperature was 300°C. 100 μL samples were injected at once using large volume on-column injection system and 250 μL volume syringe. Closure of the solvent vapour exit was indicated by the flow of carrier gas monitored by a flowmeter (ADM 2000, J and W Scientific, USA).

RESULTS AND DISCUSSION

Preliminary experiments showed that several successive extractions of phenols are needed to recover them quantitatively from aqueous samples. Low efficiency of extractions are observed when hexane is used as a solvent. Significantly better recoveries are achieved when more polar toluene is used. Dichloromethane can be also applied but it dissolves quite significantly in aqueous solutions. The solubility of hexane, toluene and dichloromethane in water at 20°C is equal to 0.0012, 0.0515 and 1.31% m/m [22], respectively. As a result, when aqueous phase is used in great excess, *e.g.* 100:1, dichloromethane is totally dissolved. The observed decrease in the organic phase volume is also significant for lower volume phase ratios (Tab. 1) and must be taken under consideration.

Table 1. Decrease of dichloromethane volume (%) in μLLE for various contents of sodium chloride in the aqueous sample and different volume ratios of the aqueous phase (V_w) to organic phase (V_o) — our experimental data

NaCl content, g / 100 g water	Decrease of dichloromethane volume, %	
	V_w:V_o = 25:1	V_w:V_o = 50:1
0	82	~100
3	62	88
35	47	51

The percentage of phenols extraction in a single micro extraction step is given in Table 2. The results indicate that the extraction efficiency decreases in the following order of solvents: dichloromethane≈toluene>hexane and with an increase in the excess of water phase. Various percentages of recovery are observed for different phenols suggesting a decrease in extraction with an increase in phenol hydrophilicity. The addition of a salting out electrolyte (NaCl) improves extraction. The effect is especially strong when hexane is used and for hydrophilic low molecular phenols, *e.g.* phenol and 4-methylphenol, for which low extraction is observed.

Table 2. Percent of phenols' recovery (R, %) in one μLLE step (1 — phenol, 2 — 4-methylphenol, 3 — 3-chlorophenol, 4 — 2,3-dimethylphenol, 5 — 4-chloro-3-methylphenol, 6 — 2,4-dichlorophenol, 7 — 2,4,6-trichlorophenol)

$V_w : V_o$	Solvent	Electrolyte content, g NaCl/100 g water	R, %						
			1	2	3	4	5	6	7
100 : 1	Hexane	0	29.4	39.1	48.1	50.4	69.7	75.4	90.1
		3	42.1	58.3	67.6	70.1	88.4	90.4	94.5
		35	61.9	82.8	85.9	88.8	90.9	92.4	97.5
	Toluene	0	67.0	84.8	92.1	92.2	95.5	95.6	96.8
		3	76.8	89.1	91.4	94.2	96.5	97.8	96.6
		35	89.6	96.7	96.5	97.1	97.9	97.2	98.1
50 : 1	Hexane	0	46.5	65.0	75.2	77.9	92.6	94.1	98.6
		3	47.4	66.9	76.8	79.3	91.4	92.5	96.5
		35	80.9	91.7	91.8	94.6	95.7	96.2	96.1
	Dichloro methane	3	80.7	100	95.1	100	94.7	100	100
		35	90.1	91.2	90.6	89.5	89.1	88.9	89.1
25 : 1	Hexane	0	52.8	74.3	77.6	81.3	92.3	92.7	89.5
		3	55.6	78.4	83.4	90.0	94.6	93.7	89.7
		35	82.9	94.2	90.1	93.0	95.1	94.5	97.8
	Dichloro methane	0	78.1	86.4	88.8	88.9	88.1	90.7	88.9
		3	91.7	95.5	94.5	95.0	100	95.9	100
		35	94.3	94.4	94.4	93.3	91.7	92.3	89.3

The precision of phenols determination (Tab. 3) is satisfactory, even if an enormous excess of the aqueous phase is used (water : toluene = 800:1). This enabled deter-

mination of the distribution coefficient with satisfactory results (Tab. 4). The exception are the data obtained for dichloromethane used for extraction and sodium chloride concentration equal to 35 g/100 mL in the aqueous feed. Due to this, these results were not discussed any further.

Table 3. Precision of phenols extraction with toluene; $V_w : V_o = 800:1$, NaCl content in aqueous solution equal to 35 g/100 g, SD — standard deviation, RSD — relative standard deviation, C.L. — confidence limit

Compound	Extraction efficiency[a], %	SD	RSD, %	C.L., $\alpha = 0.05$
Phenol	49.8	0.21	0.43	0.060
4-Methylphenol	63.6	0.31	0.48	0.075
3-Chlorophenol	64.6	1.64	2.54	0.403
2,3-Dimethylphenol	65.8	0.49	0.75	0.119
4-Chloro-3-methylphenol	66.6	0.51	0.76	0.123
2,4-Dichlorophenol	67.0	0.20	0.30	0.049
2,4,6-Trichlorophenol	67.6	0.37	0.54	0.088

[a] Average from three independent extractions.

Table 4. Logarithm of distribution coefficient D for considered phenols; 1 — phenol, 2 — 4-metylphenol, 3 — 3-chlorophenol, 4 — 2,3-dimethylphenol, 5 — 4-chloro-3-methylphenol, 6 — 2,4-dichlorophenol, 7 — 2,4,6-trichlorophenol

Solvent	Electrolyte content, g NaCl/100 g water	Logarithm of distribution coefficient D						
		1	2	3	4	5	6	7
Hexane	0	1.57	1.88	2.03	2.10	2.55	2.63	2.73
	3	1.67	2.04	2.21	2.34	2.75	2.78	2.91
	35	2.19	2.63	2.58	2.72	2.84	2.87	3.39
Dichloro-methane	0	2.71	2.96	3.05	3.06	3.02	3.14	3.06
	3	3.06	3.16	3.49	3.11	3.87	3.20	-
	35	2.94	2.97	2.95	2.88	2.82	2.84	2.76
Toluene	0	2.31	2.74	3.03	3.03	3.27	3.29	3.43
	3	2.52	2.91	3.02	3.21	3.45	3.65	3.46
	35	2.94	3.47	3.43	3.52	3.66	3.55	3.71

Linear solvation free energy relationships (LSER) are often used to correlate the extraction data [23–26]. In this case, the following combined model, which takes into account both solvent (Kamlet-Taft [27]) and solute (Abraham [28]) parameters was taken into consideration:

$$\text{Log D} = \Phi(R_2, \sum \beta_2^H, \pi_2^H, V_x (\text{or } K_{ow}), \delta_H^2, \pi^*, a, \beta) \tag{3}$$

where: δ_H^2, π^*, α, β are the solvent property parameters (δ_H^2 — cohesive energy density, MJ m^{-3}, π^* — dipolarity/polarizability, α — hydrogen bond donation and β — hydrogen bond acceptance) and R_2, $\sum \beta_2^H$, π_2^H, V_x, K_{ow} are the phenols property parameters (R_2 — solute excess molecular refraction, $\sum \beta_2^H$ — solute bond basicity, $\sum \alpha_2^H$ — solute bond acidity, π_H^2 — solute dipolarity and V_x — solute molecular volume). All parameters are given in Table 5 and were found in literature [28–30].

Table 5. Phenol acetyl derivatives property parameters (Abraham model) and solvent property parameters (Kamlet-Taft model) analysed in work [28–30]

Compound	Abraham parameters					
	R_2	$\sum \beta_2^H$	π_2^H	V_x cm^3 mol^{-1}	log K_{ow}	log K_{ow} for phenols
Phenyl acetate	0.661	1.13	0.54	113.13	1.49	1.48
4-Methylphenyl acetate	0.660	1.01	0.56	127.22	1.99	1.97
3-Chlorophenyl acetate	0.765	1.30	0.38	125.37	2.34	2.49
2,3-Dimethylphenyl acetate	0.706	1.05	0.59	141.31	2.44	2.37
4-Chloro-3-methylphenyl acetate	0.776	1.26	0.46	139.46	2.84	2.98
2,4-Dichlorophenyl acetate	0.816	1.08	0.42	137.61	2.88	2.97
2,4,6-Trichlorophenyl acetate	0.842	1.08	0.45	149.85	3.38	3.39
Solvent	Kamlet-Taft parameters					
	δ_H^2, MJ m^{-3}	π^*		β		α
Hexane	225	-0.04		0.00		0.00
Dichloromethane	400	0.82		0.00		0.13
Toluene	335	0.54		0.11		0.00

Octanol-water partition coefficient K_{ow}, calculated by the method of Hansch and Leo [31] is also used instead of molecular volume because in our opinion the solute hy-

drophobicity is better characterized by log K_{ow} than molecular volume V_x, calculated according to McGowan [32]. The latter does not take into account the effects of substituents. There was a limited data set for phenol acetyl derivatives. We found solute parameters only for phenyl acetate. The parameters for phenol acetyl derivatives were calculated according to the following relationship:

$$P_i \text{ (solute acetate)} = P_i \text{ (phenyl acetate)} + [P_i \text{ (solute)} - P_i \text{ (phenol)}] \qquad (4)$$

The following statistically valid LSER equations were obtained:
— aqueous solution does not contain the electrolyte

$$\log D = (1.39\pm0.16)\pi^* - (3.11\pm0.96)\alpha + (2.09\pm0.36)R_2 + (0.28\pm0.10)\log K_{ow} \quad (5)$$
$$n = 21 \qquad R^2 = 0.9966 \qquad SD = 0.1775 \qquad F = 1289$$

— 3 g NaCl / 100 g of water

$$\log D = (0.51\pm0.058)\log K_{ow} + (0.0054\pm0.00045) \qquad (6)$$
$$n = 20 \qquad R^2 = 0.9953 \qquad SD = 0.2099 \qquad F = 2021$$

— 35 g NaCl / 100 g of water

$$\log D = (6.06\pm0.92)\beta + (0.021\pm0.0044)V_x \qquad (7)$$
$$n = 21 \qquad R^2 = 0.9951 \qquad SD = 0.2201 \qquad F = 2017$$

where R^2 is determination coefficient, SD is standard deviation and F is Snedecor F function.

The equations (5–7) contain parameters both of solvents and solutes. The effect of solute parameters is not well defined as each derived equation contains different parameters. It can be explained by the low number of solvents. Octanol-water partition coefficient or molecular volume are the most important solute parameters which affect the extraction. Thus, the extraction depends mainly on the hydrophobicity of phenol acetyl derivatives.

The concentration of sodium chloride can be expressed in the ionic strength and general correlation derived. The preliminary computing showed that the best fitting was achieved when the ionic strength was used in the term $\sqrt{I}/(1 + \sqrt{I})$. The following statistically comparable relationships are obtained when V_x or log K_{ow} are taken into consideration:
— when V_x is used

$$\log D = -(1.51\pm0.27)\pi_2^H + (0.022\pm0.001)V_x + (1.33\pm0.09)\pi^* - (2.18\pm0.61)\alpha +$$
$$+ (0.71\pm0.09)\frac{\sqrt{I}}{1+\sqrt{I}} \qquad (8)$$
$$n = 55 \qquad R_2 = 0.9965 \qquad SD = 0.1756 \qquad F = 3104$$

— when log K_{ow} is used instead of V_x

$$\log D = (0.51\pm0.04)\log K_{ow} - (23.25\pm2.88)\pi^* + (160.42\pm18.88)\alpha + \quad (9)$$
$$+ (129.58\pm15.06)\beta + (0.71\pm0.09)\frac{\sqrt{I}}{1+\sqrt{I}}$$

n = 55 $R^2 = 0.9966$ SD = 0.1751   F = 3121

The relationships quite well fit the experimental data (Fig. 2). Moreover, the equations can be simplified with just slightly worse statistical characteristic:

— when V_x is used

$$\log D = -(1.54\pm0.30) + (0.022\pm0.001)V_x + (1.10\pm0.08)\pi^* + (0.77\pm0.09)\frac{\sqrt{I}}{1+\sqrt{I}} \quad (10)$$

n = 55 $R^2 = 0.9957$ SD = 0.1951   F = 3140

— when log K_{ow} is used instead of V_x

$$\log D = (1.85\pm0.27)R_2 + (0.51\pm0.04)\log K_{ow} - (1.12\pm0.08)\pi^* + (0.79\pm0.09)\frac{\sqrt{I}}{1+\sqrt{I}} \quad (11)$$

n = 55 $R^2 = 0.9957$ SD = 0.2047   F = 2852

The simplified equations (10) and (11) contain one solvent parameter (π^*), two solute parameters (R_2 and log K_{ow} or π_2^H and V_x) and the ionic strength and can be used to predict extraction results for other phenol acetyl derivatives.
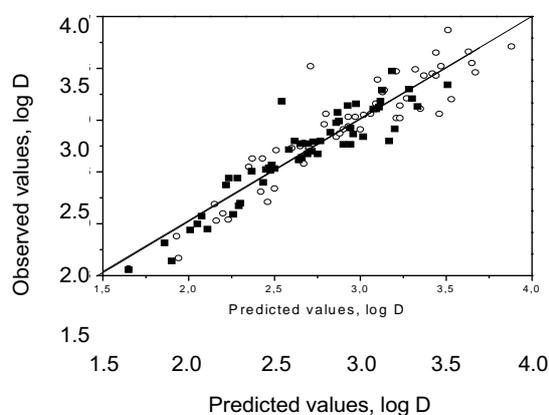
Figure 2. Comparison of experimental and predicted values of retention index for phenol acetyl derivatives
(O — eq. [8], ■ — eq. [9])

The presented experiments permitted selection of toluene as a solvent for μLLE extraction of phenol acetyl derivatives. Each of the considered phenol derivative could be totally extracted in three successive stages using even the volume ratio of the aqueous solution to toluene equal to 800:1.

Using large volume sample introduction technique (100 µL) it was possible to determine phenols at the level of 1 µg L^{-1} both in model aqueous solution and in an environmental samples taken from the river Warta in Poznan (Fig. 3) with flame ionization detector.
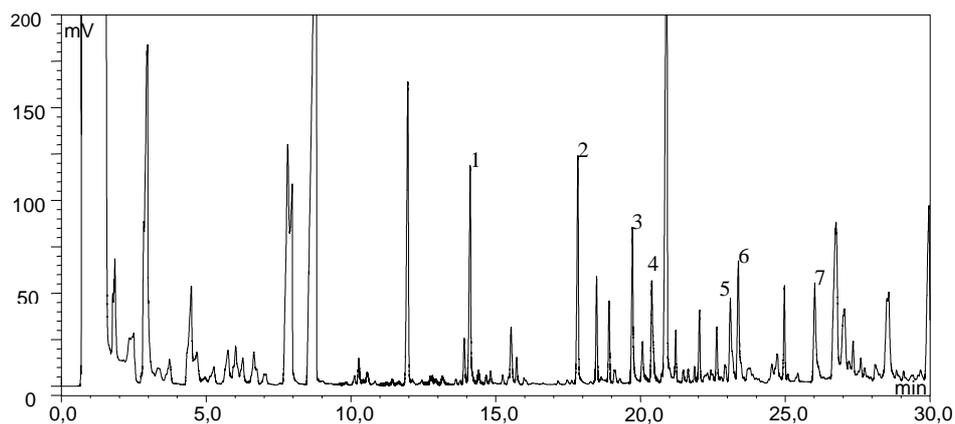
Figure 3. Chromatogram of phenol acetyl derivatives at the 4 µg L^{-1} level in environmental sample (conditions of determination in Experimental); 1— phenyl acetate, 2 — 4-methylphenyl acetate, 3 — 3-chlorophenyl acetate, 4 — 2,3-dimethylphenyl acetate, 5 — 4-chloro-3-methylphenyl acetate, 6 — 2,4-dichlorophenyl acetate, 7 — 2,4,6-trichlorophenyl acetate

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