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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Extractive Concentration of Halogen-Substituted Phenols in Their Gas-Chromatographic Determination in Aqueous Media

I. V. Gruzdev and B. M. Kondratenok

Institute of Biology, Komi Scientific Center, Ural Branch, Russian Academy of Sciences, Syktyvkar, Komi Republic, Russia

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Abstract—Method for recovery of chlorophenols from natural and drinking water for their subsequent gas-chromatographic determination was considered. Processes of microliquid extraction of bromo derivatives of chlorophenols and the method for liquid extraction with intermediate concentration of these compounds in an alkaline solution were studied.

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Phenolic compounds belong to widely occurring and foremost contaminants of natural and drinking water. The wide occurrence of phenol and its various substituted derivatives is due to their fairly good solubility in water and high reactivity [1]. Having affinity for halogens, phenols are easily chlorinated even under normal conditions to give highly toxic derivatives whose maximum permissible concentrations are 0.1 to 1.0 μg dm^{-3} [2]. For example, the main source of chlorophenols found in drinking water is the chlorination of phenol in the stage of water disinfection [3].

Chlorophenols present in drinking water are particularly hazardous because they are direct precursors of polychlorinated dibenzo-*p*-dioxins, which can be formed via chemical interaction of any two molecules of chlorinated phenols [4].

An obligatory stage of the analytical cycle in determination of phenolic compounds in aqueous solutions by gas chromatography is the extractive concentration [5]. This procedure is intended for replacing the aqueous matrix with an organic one, which is more convenient in further instrumental analysis, for raising the concentrations of the compounds to be determined, and for separating interfering components. Together with sorption, the liquid extraction belongs to the most widely used methods for concentration of phenolic compounds in their quantitative gas-chromatographic determination [6].

In the conventional variant, this procedure involves extraction at low phase ratios r = 10–100, where $r = V_{aq}/V_{org}$, and V_{aq} and V_{org} are the equilibrium volumes of the aqueous and organic phases (cm^3).

For additional concentration, the extract volume is diminished by evaporating the extractive agent in a flow of an inert gas. As a rule, this leads to distortion of the qualitative and quantitative composition of a sample being analyzed because of the loss of substances being determined and concentration of impurities contained in the extractive agent [7].

It was found that, in a 5–10-fold evaporation of hexane extracts of halogen-substituted phenols in a flow of nitrogen, the loss of compounds being analyzed reaches a value of 20–30%. In addition, the concentration ratios of the substances being determined are strongly distorted relative to those in the starting extract (Fig. 1).

In this study, it is suggested to employ alternative methods for extractive concentration of halogen-substituted phenols from aqueous media: microliquid extraction (MLE) with high phase ratios r = 500–2000 and liquid extraction with re-extraction (LE/RE).

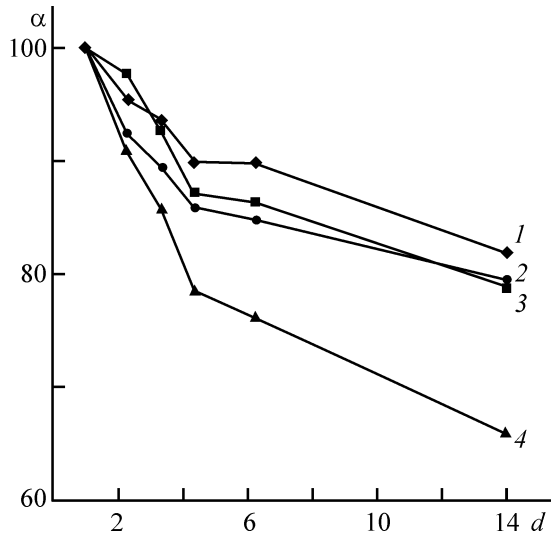

Fig. 1. Content α of halogen-substituted phenols in the extracts vs. the evaporation ratio *d*. (*1*) 2,4,6-Tribromophenol, (*2*) 2,4,6-trichlorophenol, (*3*) 2,6-dibromo-4-chlorophenol, and (*4*) 6-bromo-2,4-dichlorophenol. α, % relative to the initial amount.

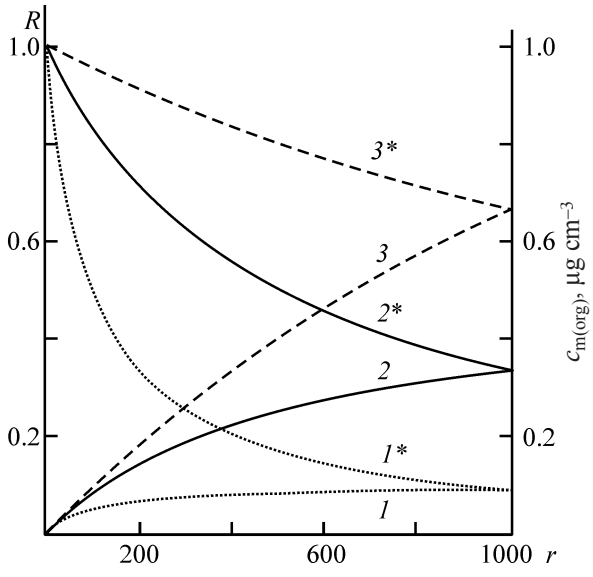

Fig. 2. (*1**–*3**) Degree of extraction, *R*, and (*1*–*3*) concentration of the substance in the organic phase, $c_{m(org)}$, vs. the phase ratio *r* at different values of *D*. *D*: (*1, 1**) 50, (*2, 2**) 500, and (*3, 3**) 2000.

EXPERIMENTAL

Chlorophenols were determined in aqueous media by a gas-chromatographic technique developed at the ecoanalytical laboratory of the Institute of Biology, Komi Scientific Center, Ural Branch, Russian Academy of Sciences [8, 9]. The method is based on obtaining bromo derivatives of chlorophenols, their extractive concentration, and subsequent gas-chromatographic determination with an electron capture detector (ECD).

Chlorophenols are brominated directly in the aqueous phase, with bromine atoms substituting hydrogen atoms in the aromatic ring in the positions 2, 4, and 6, unoccupied by chlorine atoms. Thus, phenol, monochlorophenols, and dichlorophenols yield a tribromo derivative, dibromo derivatives, and monobromo derivatives, respectively. At room temperature (20 ± 5°C), the bromination reaction ends in 40–60 s to give bromo derivatives of chlorophenols being determined in quantitative amounts.

The extractive concentration of bromo derivatives of chlorophenols was performed at phase ratios r = 10–100 in 500-cm^3 separating funnels for 5 min.

Use of the high phase ratios when performing extraction requires that the phase contact area should be made larger and their interaction be more intense. Therefore, microliquid extraction was performed in 500- and 1000-cm^3 volumetric flasks with an MM-5 magnetic stirrer (rotation frequency 5000 rpm). The equilibrium concentrations of the compounds being determined were attained in 15 min at r = 5000–1000 and in 20 min at r = 1500–2000.

Standard solutions were produced from preparations of phenol, 4-methylphenol, 2- and 4-chlorophenols, 2,4- and 2,6-dichlorophenols, and 2,4,6-trichlorophenol, all purchased from Merck (Germany).

Extracts of bromo derivatives of chlorophenols were analyzed on a Kristall 5000 gas chromatograph (Khromatek) with an ECD. The conditions of the gas-chromatographic determination were as follows: 25 m × 0.2 mm × 0.25 μm quartz capillary column (HP-5 Hewlett-Packard); carrier-gas nitrogen (special purity grade); the carrier-gas flow through the column, 0.8 cm^3 min^{-1}; flow division 1 : 50; detector gas flow 25 cm^3 min^{-1}; thermostat temperature: 160°C for columns, 320°C for evaporator, and 320°C for detector.

It follows from the liquid extraction theory [10] that an increase in the phase ratio in an extraction system leads to a decrease in the extent to which a substance being distributed is extracted into the organic phase:

$$R = \frac{D}{D + r},$$

where D is the distribution coefficient of a substance among the organic and aqueous phases.

Table 1. Distribution coefficients of chlorophenols and their bromo derivatives in the toluene–water extraction system

Chlorophenol	*D*	Bromo derivatives of chlorophenols	*D*
2,4,6-Trichlorophenol	835	2,4- Dichloro-6-bromophenol	1070
2,4-Dichlorohenol	103	2,6- Dichloro-4-bromophenol	875
2,6-Dichlorohenol	128	4-Chloro-2,6-di-bromophenol	1400
4-Chlorophenol	19	2- Chloro-4,6-di-bromophenol	1110
2-Chlorophenol	34	2,4,6-Tribromophenol	1855
Phenol	2		

Simultaneously, an oppositely directed process occurs in the system, the concentration of the substance being extracted in the organic phase increases because of the decrease in the volume fraction of the extractive agent in the system:

$$c_{m(org)} = \frac{Rm}{V_0},$$

where m is the mass of the substance being distributed in the extraction system (μg).

Figure 2 shows dependences of R and $c_{m(org)}$ on the phase ratio for substances with different distribution coefficients. It can be seen that, as D increases, the concentration of a substance in the organic phase grows substantially faster than its degree of recovery decreases.

The efficiency of extractive concentration was evaluated by the concentration coefficient K, which is the ratio between the increased concentration of the substance in the extract, $c_{m(org)}$ and its initial concentration in the aqueous phase, $c_{m(in)}$:

$$K = c_{m(org)}/ c_{m(in).}$$

It can be seen that performing efficient extractive concentration requires high values of $c_{m(org)}$. Use of microliquid extraction for concentration of hydrophilic substances is inefficient because their concentration in the organic phase remains nearly unchanged upon an increase in the phase ratio ($r > 200$) (Fig. 2, curve *1*). As, however, the distribution coefficients become larger, $c_{m(org)}$ starts

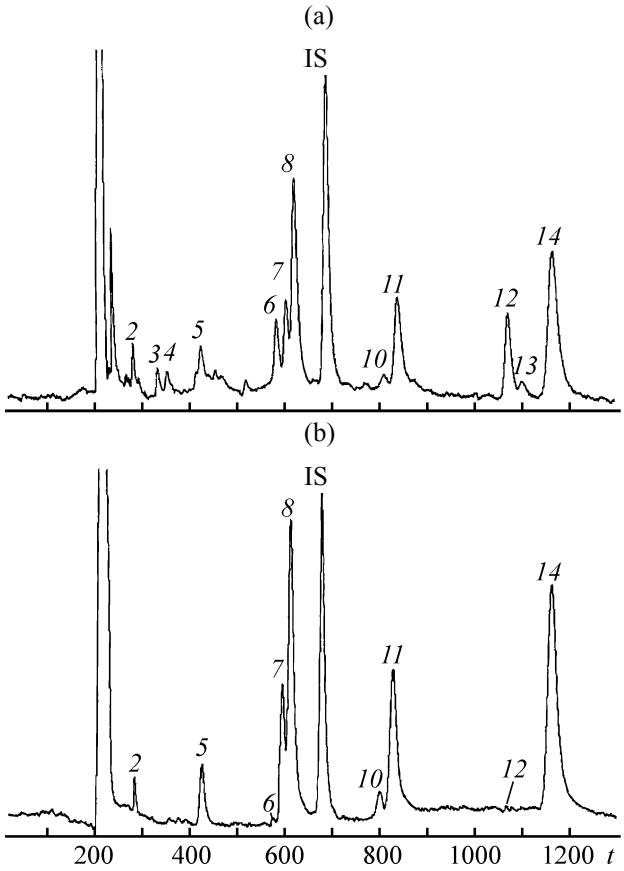

Fig. 3. Chromatograms of extracts of bromo derivatives of chlorophenols. (*t*) Retention time. (a) Variant with extract evaporation and (b) microliquid extraction. (*5*) 2,4,6-Trichlorophenol, (*7*) 6-bromo-2,4-dichlorophenol, (*8*) 4-bromo-2,6-dichlorophenol, (*10*) 2,6-dibromo-4-chlorophenol, (*11*) 4,6-dibromo-2-chlorophenol, (*14*) 2,4,6-tribromophenol, (*1, 4, 6, 12, 13*) unidentified components. IS, internal standard (2,6-dibromo-4-methylphenol).

to noticeably grow in this interval (Fig. 2, curve *2*), and, for substances with $D > 2000$, increases nearly in a direct proportion to the phase ratio r (Fig. 2, curve *3*). Thus, for highly hydrophobic substances, an increase in the phase ratio does not impair the efficiency of the extractive concentration and the choice of r is only restricted by technical difficulties in performing MLE and by the growing time required for equilibrium concentrations of the compounds being determined to be attained.

The method used to determine chlorophenols in aqueous media involves their chemical modification to bromo derivatives [8, 9]. Introduction of bromine atoms into molecules of chlorophenols results in a substantial increase in their distribution coefficients [11, 12], which have values of 800 to 2000 in the water–toluene system

Table 2. Degrees of extraction (R), concentration coefficients H, and detection limits cm(min) of bromo derivatives of chlorophenols in LE/ER and MLE

Substance	*R*, %		*K*		$c_{m\,(min)}$, μg dm^{-3}	
	MLE (*r* = 1000)	LE/RE (*r* = 50)	MLE	LE/RE	MLE	LE/RE
2,4,6- Trichlorophenol	45.5	94.4	455	755	0.1	0.009
2,4- Dichloro-6-bromophenol	51.7	95.5	517	764	0.08	0.007
2,6- Dichloro-4-bromophenol	46.7	94.6	467	757	0.09	0.007
4-Chloro-2,6-dibromophenol	58.3	96.6	583	772	0.06	0.006
2- Chloro -4,6- dibromophenol	52.6	95.7	526	766	0.07	0.006
2,4,6- Tribromophenol	65.1	97.4	650	779	0.05	0.005

(Table 1). The high values of the distribution coefficients of bromo derivatives of chlorophenols enable use of the microliquid concentration variant in the analytical cycle of chlorophenol determination.

Application of MLE not only makes it possible to provide high concentration coefficients, but also improves the selectivity of determination of highly hydrophobic compounds being analyzed. For example, extraction at low phase ratios ($r < 100$) results in that the concentrations of all the compounds in the organic extract will be close, irrespective of their distribution coefficients (Fig. 2). In MLE ($r = 1000$), the concentrations of highly hydrophobic compounds in the extract will exceed those of hydrophilic substances by one to two orders of magnitude.

Figure 3 shows chromatograms of extracts of bromo derivatives of chlorophenols, produced by the conventional concentration technique at $r = 50$, with the subsequent evaporation of the extractive agent (Fig. 3a) and microliquid extraction at $r = 1000$ (Fig. 3b). The volume of the aqueous sample was 1 dm^3; in the first case, the extraction was performed with 20 cm^3 of toluene, with the subsequent evaporation of the extract to 1 cm^3; in the second case, 1 cm^3 of toluene was used.

The chromatographic peaks of bromo derivatives of chlorophenols, obtained in the variant with extract evaporation (Fig. 3a), have a lower intensity, which is due to the evaporation loss and impossibility of complete separation of the extract from the aqueous phase. In addition, the chromatogram shows peaks of substances that are not present in the extract obtained using MLE (Fig. 3b). Apparently, they belong to more hydrophilic components or impurities contained in the extractive agent and concentrated upon evaporation.

The microliquid extraction was used to determine chlorophenols in potable, natural, and waste water (concentration range 0.2–5 μg dm^{-3}).

For a higher sensitivity determination of chlorinated phenols in thaw, rain, and ground water (concentration range 0.02–0.5 μg dm^{-3}), another variant of extractive concentration was used: liquid extraction with a re-extraction. This technique involves liquid extraction at low phase ratios ($r = 10$–100), subsequent re-extraction of bromo derivatives of chlorophenols into an alkaline solution, removal of most part of the organic solvent, and repeated extraction upon neutralization of the alkaline solution.

The re-extraction into an alkaline solution is based on the fact that phenolic compounds exhibit properties of weak organic acids. For example, in agitation of an aqueous phenol solution mixed with an organic solvent, a complex equilibrium is attained [13]:

$$[C_6H_5OH]_{org} \rightleftarrows [C_6H_5OH]_{hydr} \underset{\text{Acidification}}{\overset{\text{Alkalization}}{\rightleftarrows}} C_6H_5OH^- + H^+$$

In a strongly acidic medium, the equilibrium in both reactions is shifted to the right. Because charged phenolate ions are hydrated to a considerably greater extent than phenol molecules and are not extracted, they nearly quantitatively and irreversibly pass from the organic solvent into the alkaline solution.

Compared with MLE, including the liquid extraction with re-extraction into the analytical cycle gives the following advantages (Table 2): (1) bromo derivatives of the chlorophenols being analyzed are nearly quantitatively recovered and the maximum possible concentration coefficients for the given system are reached; (2) the obtained concentration coefficient is the same for all the phenols being extracted ($K_{av} \sim 765$) and depends on D to a lesser extent; (3) the reliability of the results increases because the probability that the extract contains just phenolic compounds substantially increases on

performing re-extraction; and (4) a smaller amount of interfering components is present in the extract because it contains only organic acids.

As a result, LE/RE makes it possible to diminish by a factor of 10–15 the detection limit of the chlorophenols being analyzed. However, this procedure requires a longer sample preparation time and a greater expenditure of reagents and organic solvents.

The study demonstrated that, in extractive concentration of phenolic compounds with $D > 500$, the conventionally employed concentration can be replaced with microliquid extraction. Values of D can be made higher by choosing the most effective extractive agent, using salting-out agents, and introducing hydrophobic substituents into the compounds being distributed [13]. Trace amounts of phenols in water can be determined by liquid extraction with re-extraction, which involves intermediate concentration of the compounds being determined in an alkaline solution.

Both the variants of liquid extraction under consideration make it possible to reach high concentration coefficients for compounds being determined and do not require evaporation of an organic solvent, a stage distorting the qualitative and quantitative composition of a sample being analyzed.

CONCLUSIONS

(1) Phenolic compounds (bromo derivatives of phenol, 2- and 4-chlorophenols, 2,4- and 2,6-dichlorophenols, and 2,4,6-trichlorophenol) were concentrated by a microliquid variant of extraction, with phase ratios r = 500–2000, and by liquid extraction with re-extraction, in which phenol are extracted at r = 10–100 with intermediate concentration in an alkaline solution.

(2) The extractive concentration methods used in the study were theoretically substantiated and the optimal conditions for these techniques were determined.

(3) It was shown that exclusion of the stage of evaporation of the organic solvent from the analytical cycle leaved undistorted the information about the qualitative and quantitative composition of a sample.

(4) A high efficiency of these methods of extractive concentration in gas-chromatographic analysis of trace amounts of chlorophenols in various water bodies was demonstrated.

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