Extraction-Voltammetric Determination of Dihydroxybenzenes in Aqueous Solutions Using Organic Oxides

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Abstract

The paper studied some regularities of extraction of dihydroxybenzenes (DHB) using toluene organic solutions of amine and phosphine oxides with the purpose of extraction concentration and determination of trace amounts in aqueous solutions. Distribution coefficients of DHB between toluene solutions of organic oxides and water versus the position of OH group in the molecule and the donor ability of oxides were determined. Pyrocatechin has higher extraction characteristics than resorcin and hydroquinone. The maximum distribution coefficients of DHB were reached, which provided their 95–97 % extraction from aqueous media at 50-fold concentration and single extraction. A method for determination of trace amounts of DHB (10^{-7}–10^{-5} mol/dm³) in water samples with pre-concentration with toluene solutions of trioctylphosphine and trioctylamine oxides (0.5–0.7 mol/dm₃) followed by voltammetric detection in extract with a glassy carbon electrode (GCE) against acetonitrile and a solution of sodium perchlorate in isopropyl alcohol was developed. The current-voltage curves reflecting the kinetics of oxidation of analytes in a disk GCE at voltammetric detection of DHB in the organic phase were obtained. Calibration curve method was used for quantitative voltammetric determination of each isomer in individual solutions or binary mixtures of catechol, resorcin, and hydroquinone, resorcin, and also total DHB (in terms of pyrocatechin) in an extract. The level of reliable determination of DHB concentrations is 0.5–1 MPC; relative error does not exceed 5 %. A method for total determination of DHB, and also each isomer in individual samples or binary mixtures of pyrocatechin and resorcin, and hydroquinone and resorcin is recommended for use in analytical laboratories for monitoring the quality of natural and treated waste water.

Key words: dihydroxybenzenes, organic amine and phosphine oxides, extraction concentration, voltammetry

INTRODUCTION

Dihydroxybenzenes (DHB) are common pollutants of natural and waste water. The DHB that consume large amounts of oxygen during oxidation are contained in waste water of coke chemical, pharmaceutical enterprises, factories for the production of photographic materials, organic dyes [1, 2]. Mutagenic and cancerogenic effects of DHB on living organisms have been proven experimentally [3, 4].

Phenols are unequal with respect to their toxicologic and organoleptic actions. Volatile phenols (phenol, cresols, xylenols, *etc.*) are more toxic, compared to non-volatile (resorcin, pyrocatechin, hydroquinone, pyrogallol and other polyhydric phenols), therefore their allowable concentrations in water reservoirs are extremely small. However, for fishery purposes, MPC of resorcin and hydroquinone in water are 0.001 and 0.004 mg/dm₃, respectively [5], which requires their selective determination (Table 1).

Quantitative assessment of environmental safety of water resources is relevant analysis problem. Reliable determination of DHB in aqueous media at a level of MPC (0.1–0.2 mg/dm³) includes the pre-concentration stage [1]. Dihydroxybenzenes are present in the environment at

TABLE 1

Physicochemical indicators of dihydroxybenzenes (DHB)

Dihydroxibenzenes (DHB)	Solubility in water, g/dm^3	MPC, mg/dm^3	MPC, mg/dm^3 (in fisheries)	pK_a
Hydroquinone	59.0	0.2	0.001	9.9
Resorcin	229.0	0.1	0.004	9.2
Pyrocatechin	45.1	0.2	0.100	9.4

trace amounts, therefore it is advisable to use joint analysis methods that include various techniques of pre-concentration (liquid extraction, sorption, electro-concentration) followed by DHB detection using highly sensitive physicochemical methods.

Liquid extraction by non-aqueous systems is an efficient method of concentration of organic compounds. As a rule, the distribution coefficients (DC) of DHB between conventionally used organic extractants and water are low [6] and do not ensure the complete transition of components into extract [7]. Almost complete recovery is reached only during triple extraction and 2−4-fold concentration during extraction of dioxobenzene with methyl *tert*-butyl ether [8]. Tributylphosphate that is the most efficient extractant for the concentration of DHB ensures DC of 45 in hexyl alcohol during single extraction and extracts no more than 85 % of DHB [7]. A method for determination of DHB in aqueous solutions by reversed-phase microcolumn high-performance liquid chromatography with preliminary acetonitrile extraction/partitioning is characterised by a high degree of extraction (98 %), however, requires the use of complex equipment and a large amount of a salting-out agent that is ammonium sulphate (36.5−40.0 mass % towards the sample mass) [9, 10].

Organic phosphorus- and nitrogen-containing oxides [11−14], the use of which allows reaching distribution coefficients and the degrees of extraction of analytes from aqueous media (to 98 %) with single-use extraction, have proven themselves as efficient extractants for phenol compounds and aromatic amines. Herewith, the consumption of salting-out agents is decreased by several times.

To determine phenolic compounds at a level of trace concentrations electroanalytical analysis methods, such as polarography, voltammetry, potentiometry, amperometry *etc.*, are used. Oxidation reactions of DHB to appropriate quinones include electron transfer, which allows using, for example, voltammetry for obtaining information about the progression of reactions. Using this method, one can determine low concentrations of DHB in aqueous media [15, 16], however, defining them at a level of the MPC without pre-concentration and separation from interfering components is rather a complicated task [17].

Known techniques for determination of DHB are insufficiently selective and quite time-consuming since complex and expensive instruments [10] or special modified electrodes [17−20] are required for their use.

Voltammetric determination of DHB with their joint presence in solutions has not been sufficiently elucidated in the literature. This is particularly true for their determination in organic solvents. The development of techniques aimed at separate voltammetric determination of DHB in extracts is of both scientific and practical interest for analytical practice.

Work purpose is the development of a technique for voltammetric determination of DHB in aqueous media with preliminary extraction concentrating using toluene solutions of organic oxides, such as trioctylphosphine and trioctylamine.

The following tasks were solved towards the realisation of the established goal:

− the study of regularities in the extraction of pyrocatechin, resorcin, and hydroquinone with trioctylamine and trioctylphosphine oxides;

− selection of an effective extraction system for concentrating DHB;

− voltammetric determination of DHB in extract;

− the development of a technique for voltammetric determination of DHB in aqueous media in their joint presence.

EXPERIMENTAL

Extraction of pyrocatechin, resorcin, and hydroquinone with toluene solutions of trioctylphosphine oxide (TOPO) and trioctylamine oxide (TOAO) was explored. The first compound was obtained by recrystallization from commercial heptane; TOAO was synthesized at the Institute of Inorganic Chemistry of SB RAS (IIC SB RAS). The solubility of the oxides is maximum in toluene medium (0.7 mol/dm^3). Furthermore, rela-

tively high distribution coefficients compared to other solvents were acquired because of lower association of oxides in toluene during extraction of phenol compounds by toluene solutions of oxides [11].

Interphase separation of DHB in concentrations ranging between $(2 \cdot 10^{-4}) - (2 \cdot 10^{-2})$ mol/dm^3 was studied in an acid medium (pH 2−3) at (20±0.1) °C; centrifugation was used to improve phase separation.

The content of analytes in equilibrium aqueous solution during the determination of characteristics of DHB was found photometrically in the UV spectral region at 275 nm, 273 nm, and 288 nm for pyrocatechin, resorcin, and hydroquinone, respectively.

Determination of DHB in the equilibrium organic phase was carried out voltammetrically by preliminary dilution of the analyzed extract with acetonitrile in 1 : 1 ratio and the addition of a saturated solution of sodium perchlorate (0.2−0.3 cm^3) in isopropyl alcohol as the background electrolyte. Measurements were performed using LP-7 polarograph (Czech Republic) in the constant current mode of voltamperograms with the linear potential sweep with 200 eV/min rate. Detector cell is a three-electrode system (VED-1, Kuban State University): the main electrode is a glassy carbon disk electrode (GCE) with a 4 mm diameter, the auxiliary is cell glassy carbon; a reference electrode is a saturated silver chloride electrode. Surface preparation of the main electrode consisted in careful mechanical and electrochemical treatment. Grinding and polishing of GCE were performed using abrasive paper with different porosity Al$_2$O$_3$. To assess mechanical treatment quality an optical microscope was used. Afterwards, ultrasound treatment with distilled water was carried out in ultrasound field for 10 min and GCE surface was activated in a 0.1 mole/dm^3 H$_2$SO$_4$ solution by scanning of potentials with the linear sweep in a (−1) − 2.5 V region. Electrode surface was carefully rinsed with a 20 % EtOH solution with stirring for 3−5 min after each measurement cycle to remove reaction products.

The content of DHB in the organic part was defined by the calibration curve method constructed by standard solutions of chemically pure preparations in toluene/acetonitrile solution in 1:1 ratio. A precise sample weight of DHB for the initial solution of DHB was dissolved in acetonitrile and used for 3−4 days. Standard solutions were prepared by dissolution of the initial solution with acetonitrile in the presence of background electrolyte directly prior to voltamperogram registration.

The concentration of DHB in the analysed aqueous solution (C, mg/dm^3) was calculated by the formula:

$$C = C_0 \cdot 100\%/R$$

where C_0 is the concentration of DHB in extract found by the calibration graph, mg/dm^3; R is the degree of extraction of DHB in the system of the toluene oxide solution − aqueous solution", %.

The degree of extraction of DHB was calculated by the formula:

$$R = DC \cdot 100/(DC + V/V_o)$$

where DC is the distribution coefficient of DHB in the system of toluene oxide solution − aqueous solution; V/V_o is the ratio of volumes of aqueous and organic phases, respectively.

RESULTS AND DISCUSSION

Regularities of extraction of DHB

Strong intermolecular hydrogen bonds that contribute to the transfer of substances into the non-aqueous phase arise during extraction of DHB [11]. The latter with electron donor solutions of organic oxides (L) can be represented by the scheme:

$$m(\text{DHB}) + s\text{L} \rightarrow (\text{DHB})_m\text{L}_s$$
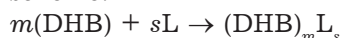
where m and s are the number of molecules of extractant and DHB in the formed complex.

Comparative extraction characteristics of DHB (DC, R) in systems with TOAO are higher, compared to TOPO (Table 2), which correlates with the data of the donor ability of oxides [11].

DC of DHB versus the position of the OH group in a molecule was found (Fig. 1). Pyrocatechin differs from resorcin and hydroquinone by higher extraction characteristics (*ortho*-effect).
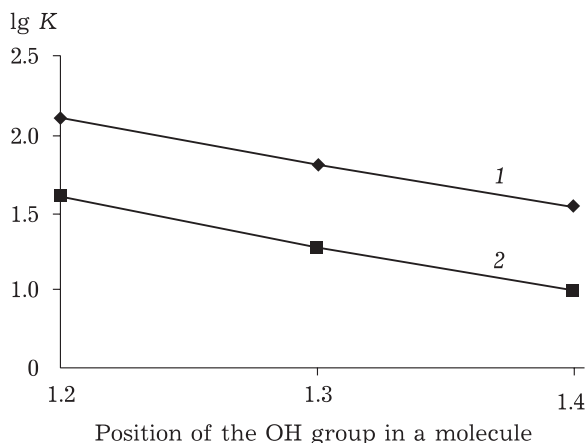

Fig. 1. Distribution coefficients of DHB versus the position of the OH group in a molecule during extraction with toluene solution of TOAO (*1*) and TOPO (*2*).

TABLE 2

Distribution coefficients and extraction degree of dihydroxybenzenes with toluene solutions of oxides
(V_w/V_s = 20 : 2; the concentration of oxides is 0.1 mole/dm^3; n = 3; P = 0.95)

Oxides	Pyrocatechin		Resorcin		Hydroquinone	
	DC	$R, \%$	DC	$R, \%$	DC	$R, \%$
TOPO	130±8	92.9	65±5	86.7	35±4	77.8
TOAO	460±10	97.9	320±8	97.0	110±7	91.7

An intramolecular hydrogen bond in the pyro-catechin molecule increases isomer hydrophobicity and contributes to its transfer to extract. The values of DC for pyrocatechin are higher than for strongly hydrated resorcin, since its solubility in water is 5 times higher (Table 1) than that of *ortho*-isomer [21].

Concentration of DHB

An opportunity for the use of toluene solutions of TOAO for extraction and concentration of DHB from aqueous media was studied. The data of extraction concentration of pyrocatechin, resorcin, and hydroquinone with toluene solutions of TOAO under comparable conditions with the ratio of volumes of aqueous and organic phases of 100 : 2 were obtained (Table 3). The maximum values of DC that ensure 95−97 % extraction of DHB with 50-fold concentration and single extraction were reached.

The findings of extraction concentration of DHB are applicable for the development of a technique for determination of their trace amounts in aqueous media with voltammetric detection in the organic phase.

Voltammetric detection of DHB in an extract

Dihydroxybenzenes are oxidized over GCE in the positive region of potentials. The curves reflecting the kinetics of oxidation of analytes over a microdisc GCE were obtained during voltammetric detection of DHB in toluene/acetonitrile solution (Fig. 2). Clear and well reproducible analytic signals of DHB in individual solutions were obtained over an activated GCE.

It was found that the half-wave potentials ($E_{1/2}$) of oxidation of pyrocatechin and hydroquinone over GCE were different by 0.100 V, and $E_{1/2}$ for resorcin was 1.18 V. Electroactive substances of the organic background (TOAO, sodium perchlorate) are discharged at $E_{1/2}$ > 1.8 V, which does not prevent determination of DHB in the organic phase.

The findings can be used for quantitative voltammetric determination of each isomer in individual solutions or binary mixtures of pyrocate-chin/resorcin and hydroquinone/resorcin, and also total DHB in aqueous media. Voltammograms of oxidation of analytes in binary mixtures of pyrocatechin/resorcin and hydroquinone/resorcin in different ratios, and also in a mixture of three DHB are presented in Fig. 3. Oxidation of hydroquinone and pyrocatechin over GCE is expressed by one wave in a voltammogram (curve 5), oxidation of resorcin − by a separate wave at $E_{1/2}$ = 1200 mV.

We did not manage to improve the separation of peaks of hydroquinone and pyrocatechin in the surface of GCE. It is almost impossible to increase the distance between peaks by selection of pH values of background electrolytes since the peak potentials of oxidation-reduction of the studied isomers change proportionally to the pH value with the identical interval [22].

Difficulties of selective determination of dioxybenzene isomers are related to the closeness of their chemical properties, therefore additional techniques of their separation by extraction or chromatography are required. Selective determination of each of the isomers with their joint presence in a solution by the voltammetric method is a complex task. Nevertheless, different positions of two hydroxyl groups in the benzene ring drive different rates of their oxidation reactions that are decreased in the row: hydroquinone > pyrocatechin > resorcin. Hydroquinone is subjected to oxidation most readily, then − pyrocatechin and resorcin (Fig. 2), which is consistent with known data [23, 24].

A dependence of the wave height (diffusion current) on the concentration of dioxybenzene isomers in the organic phase $h = f(C)$ that is described by regression equations with relatively high approximation reliability was obtained for quantitative determination of DHB in individual and binary solutions (Table 4). The range of linearity of calibration graphs over GCE is $(5 \cdot 10^{-3}) − (1.5 \cdot 10^{-1})$ mg/cm^3, which meets the requirements on the suggested content of DHB in an extract. The results are well reproduced, there is no systematic error. The detection limit of DHB in the organic phase is $1 \cdot 10^{-3}$ mg/cm^3.

TABLE 3

Distribution coefficients and degree of extraction of dihydroxybenzenes with TOAO solutions in toluene (V_w/V_s = 100 : 2; n = 3; P = 0.95)

Hydroxybenzene	TOAO concentration, mole/dm^3					
	0.3		0.5		0.7	
	DC	R, %	DC	R, %	DC	R, %
Pyrocatechin	1200±25	96.0	1350±25	96.4	1600±50	97.0
Resorcin	900±20	94.7	1150±23	95.8	1300±25	96.3
Hydroquinone	630±10	92.7	820±15	94.3	1000±20	95.2

The analytic signal in GCE and the slope angle of the calibration graph when determining hydroquinone is higher than for isomers with other identical conditions (see Table 4). Perhaps, the nature of extractant − TOAO that is characterised by a high electron donor ability plays a role in a relatively complex extraction system. When determining the composition of the extracted complex it was earlier found by us that pyrocatechin and resorcin complexes contain one TOAO molecule (1 : 1), hydroquinone complex-

es − two [11]. The presence of two amine oxide molecules in hydroquinone extract contributes to its active discharging in GCE. Current strength values for the other two isomers are almost identical.

A technique for determination of trace amounts of DHB (10^{-7}−10^{-5} mole/dm^3) in aqueous samples that includes pre-concentration of DHB with toluene solutions of TOPO or TOAO (0.5−0.7 mole/dm^3) by voltammetric detection in extract with GCE with addition of acetonitrile (in
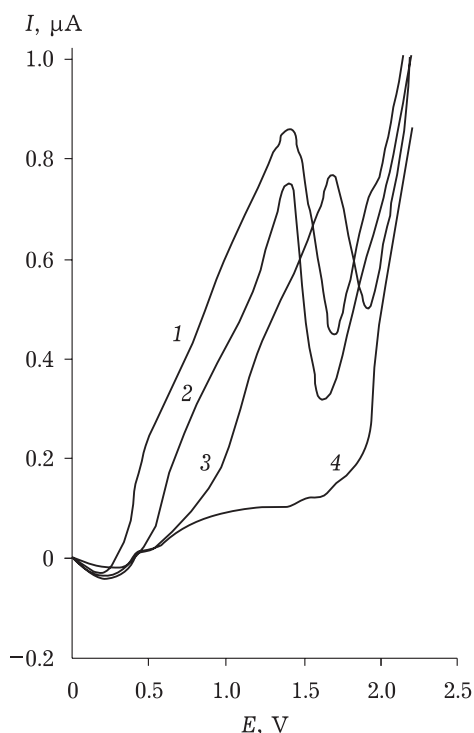

Fig, 2. Voltammograms of DHB oxidation (C_{DHB} = 9 · 10^{-2} mg/cm^3) over a glassy carbon electrode in toluene-acetonitrile solutions in the presence of TOAO and sodium perchlorate: *1* − hydroquinone, *2* − pyrocatechin, *3* − resorcin, *4* − background of 0.1 mol/dm^3 alcohol solution of NaClO$_4$ + toluene-acetonitrile (1 : 1) solution of TOAO (0.7 mole/dm^3).
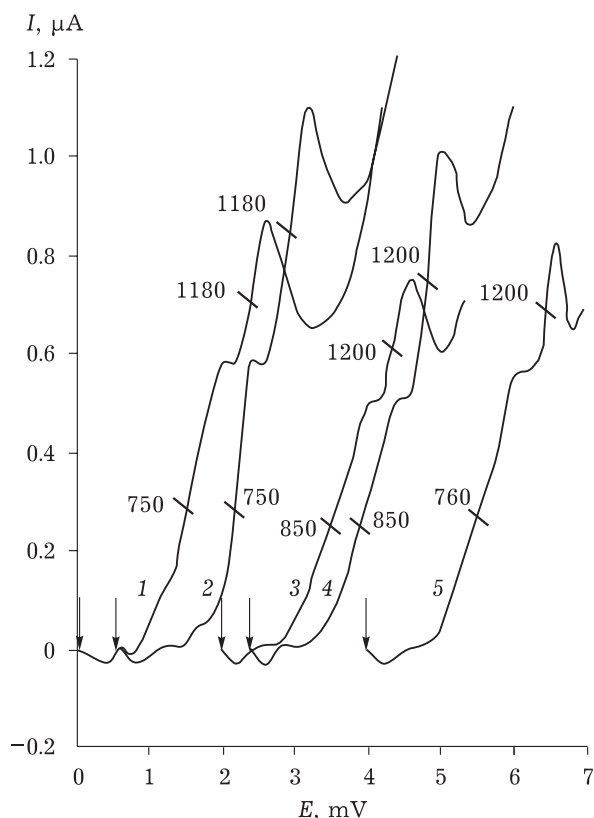
Fig. 3. Voltammograms of DHB oxidation in binary mixtures over a glassy carbon electrode (GCE) in the organic phase: *1* − 0.06 mg/cm^3 of hydroquinone + 0.03 mg/cm^3 of resorcin, *2* − 0.06 mg/cm^3 of hydroquinone + 0.06 mg/cm^3 of resorcin, *3* − 0.06 mg/cm^3 of pyrocatechin + 0.03 mg/cm^3 of resorcin, *4* − 0.06 mg/cm^3 of pyrocatechin + 0.06 mg/cm^3 of resorcin, *5* − a mixture of three DHB by 0.3 mg/cm^3 of each isomer.

TABLE 4

Coefficients of the regression equations for the dependence $h = f(C)$ in oxidation of dihydroxybenzenes over a glassy carbon electrode (GCE) in the toluene/acetonitrile solution

Hydroxybenzenes	Regression equation: $Y = aX + b$		
	a	b	R^2
Pyrocatechin	174.04	7.6970	0.9998
Resorcin	127.04	7.5097	0.9996
Hydroquinone	121.34	7.3409	0.9993

the ratio with extract of 1 : 1) against the background of a saturated solution of sodium perchlorate in isopropyl alcohol was developed by experimental results.

When determining the total content of DHB content in the organic phase the total amounts of hydroquinone and pyrocatechin were accessed by the wave length (*e.g.* Fig. 3, curve *5*) and calculated by the regression equation in terms of pyrocatechin. Resorcin concentration was defined by wave 2 length value and accordingly to the regression equation for this isomer.

Extraction-voltammetric determination of DHB in aqueous solutions was carried out. The reproducibility and correctness of determination results were assessed by the "introduced-found" method for 48 samples with the concentrations of $5 \cdot 10^{-2}$ and $1 \cdot 10^{-1}$ mg/dm^3 by 4 samples of aqueous solutions of each DHB, binary mixtures of catechol/resorcin, and hydroquinone/resorcin and a mixture of three isomers for each concentration. Statistically processed data of the total determination of DHB (in terms of pyrocatechin) and in binary mixtures of pyrocatechin/resorcin and hydroquinone/resorcin are given in Table 5. Reliable determination level of DHB concentrations is 0.5−1 MPC; the relative error of the determination does not exceed 5 %.

CONCLUSION

An opportunity for individual determination of resorcin in the presence of pyrocatechin or hydroquinone, and also all isomers in individual solutions was demonstrated. A technique for total determination of DHB, and also all isomers in individual samples or binary mixtures of pyrocatechin/resorcin and hydroquinone/resorcin is recommended for the use in analytical laboratories that monitor the quality of natural and treated waste water. It allows monitoring the content of DHB in treated waste water of painting and photographic enterprises.

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TABLE 5

Results of extraction-voltammetric determination of dihydroxybenzenes in aqueous solutions ($n = 4$; $P = 0.95$)

Hydroxybenzenes	Introduced, $C \cdot 10^2$, mg/dm^3	Found, mg/dm^3					
		$\overline{C} \cdot 10^2 \pm \Delta$	S_r	$\overline{C} \cdot 10^2 \pm \Delta$	S_r	$\Sigma\overline{C} \cdot 10^2 \pm \Delta$	S_r
Pyrocatechin	5.0	4.85±0.19	0.0263	−	−		
	10.0	9.78±0.13	0.0085	−	−		
Resorcin	5.0	4.90±0.26	0.0326	4.82±0.23	0.023	14.85±0.36	0.015
	10.0	9.68 ±0.30	0.0205	9.67±0.20	0.013	28.97±0.30	0.007
Hydroquinone	5.0	−	−	5.20±0.30	0.036		
	10.0	−	−	10.2±0.41	0.025		

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