ISSN 1061-9348, Journal of Analytical Chemistry, 2018, Vol. 73, No. 6, pp. 551–559. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © N.S. Brilenok, M.V. Bakhareva, V.I. Vershinin, 2018, published in Zhurnal Analiticheskoi Khimii, 2018, Vol. 73, No. 6, pp. 446–454.

ARTICLES

UV-Spectrometric Determination of Total Phenols Using Diazotized Sulfanilic Acid

N. S. Brilenok[a], M. V. Bakhareva[a], and V. I. Vershinin[a, *]

[a] *Omsk Dostoevsky State University, Omsk, 644077 Russia*

**e-mail: vyvershinin@yandex.ru*

Received June 27, 2017; in final form, December 17, 2017

Abstract—Phenolic compounds, including nitro- and chlorophenols, in neutral aqueous solutions react with diazotized sulfanilic acid. The molecular absorption coefficients of azo dyes obtained from various phenols in the range 360–380 nm are quite close, which ensures the determination of the total concentration of phenols as C_6H_5OH. Under optimized conditions, the systematic errors in the analysis of model mixtures did not exceed 30 rel. %. They may be due to either the difference in molar absorption coefficients, or the delayed formation or instability of some azo dyes, and also due to the influence of reducing agents and arylamines. The procedure may become a good alternative to the determination of the phenolic index of sewage waters by the reaction with 4-aminoantipyrine.

Keywords: UV-spectrometry, phenols, azo coupling, sulfanilic acid, analysis of natural and waste water, systematic errors

DOI: 10.1134/S1061934818060047

Many phenols are strong toxicants. Thus, the MPC of the simplest phenol C_6H_5OH in natural waters is only 1 μg/L [1]. As a rule, phenolic contamination of water reservoirs is monitored without separating phenol mixtures and not separately determining them. To evaluate the total concentration of phenols (c_Σ), they are converted to the same type of colored compounds, the total analytic signal A_Σ (the absorbance of the mixture of reaction products at a selected wavelength λ) is measured, and the total index is calculated from the calibration curve constructed for C_6H_5OH solutions. Usually phenols are converted into quinoneimine dyes by reacting with 4-aminoantipyrine (**4-AA**) [1, 2]. The result of such an analysis (c^*), expressed in terms of C_6H_5OH, is called the phenolic index (**PI**) and is considered an approximate estimate of c_Σ. The procedures of determining PI in recent years have been severely criticized, because

—not only phenols enter the reaction with 4-AA, but also some non-phenolic compounds, the signals of which are superimposed on the signals of phenols [3];

—not all phenols enter into the reaction with 4-AA: according to the data of [4], under the conditions of the determination of PI with 4-AA, five of sixteen tested phenols reacted; *para*-cresol and other phenols, in which the *para*- position is occupied by alkyl-, aryl-, or nitro groups, did not react [2];

—the sensitivity coefficients in determining various phenols with 4-AA for any given value of λ are very different, which results in great differences between c^* and c_Σ [5];

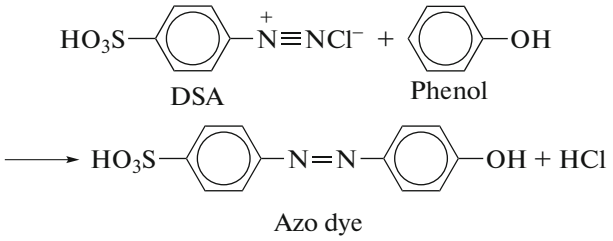
—by the reaction with 4-AA, C_6H_5OH is determined with a higher sensitivity than the other phenols [6], which contradicts the theoretical recommendations for the selection of a standard substance [7] and results in strongly underestimated c_Σ. Because of this, in the United States, PI is considered to be the lower boundary of the true value c_Σ [6]. The operation of steam distillation included in many procedures results in losses of unstable compounds, e.g., biatomic phenols and aminophenols [8], which should further lead to the underestimation of the result of the analysis.

The developers of normative documents [9–11] gave in them the accuracy figures of standard procedures for the determination of PI. The limiting values of systematic errors calculated from these figures are from 5 to 20 rel. %, depending on the value of PI. These values seem to be underestimated. The actual errors are unpredictable, because they are subject the composition of a phenol mixture in a single sample.

It should be noted that the results of PI determination are usually several times lower than the results of analysis of the same waters by HPLC [12]. Obviously, the use of PI may result in a dangerous underestimation of the degree of pollution of water bodies [13]. Some experts propose abandoning of the spectrometric method altogether in determining the amount of phenols, replacing it by GLC or HPLC [4]. However, the procedures of the chromatographic determination

of c_Σ have their own problems and limitations [1, 14]. We believe that the possibilities of the spectrometric estimation of c_Σ are far from being exhausted; it is only necessary to replace 4-AA with a more suitable reagent.

Azo coupling of phenols with diazotized sulfanilic acid (**DSA**) gives azo dyes, having relatively high (~2×10^4) molar absorption coefficients [15]. In determining individual phenols [16], the reactions proceed according to the scheme:



The same reactions may be used to determine total phenols [17]; however, the corresponding procedure needs to be specified and thoroughly tested.

The ultimate aim of our study was to develop a rapid procedure that provides a correct assessment of the phenolic pollution of water bodies. The aim of the first stage was the optimization of the conditions for the interaction of phenols with DSA and testing a possibility of using DSA for the determination of the sum content of phenols in model solutions. In this paper, the results of studies carried out using single- and multicomponent model solutions are presented. The results of analysis of various types of sewage waters will be presented and discussed in the next paper.

EXPERIMENTAL

Nine model compounds were used: the simplest phenol (**Ph**), *ortho*-, *meta*-, and *para*-cresols (**OC**, **MC**, and **PC**), guaiacol (**Gu**), resorcinol (**R**), 1-naphthol (**N**), *ortho*-chlorophenol (**CPh**), and *para*-nitrophenol (**PNPh**). Aqueous or alcoholic–aqueous solutions of these substances with a concentration of 0.0100 M were prepared from accurate weight portions of chemically pure reagents. Working solutions were prepared by diluting stock solutions with distilled water in the day of analysis. Model mixtures (aqueous solutions containing from 2 to 5 phenols in comparable concentrations of the order 10^{-5} M) were prepared from working solutions of individual phenols and analyzed in the day of preparation. A DSA solution (5×10^{-3} M) was prepared according to the procedure described in [16].

To transfer phenols to azo dyes, a necessary volume of a working solution of a phenol under investigation or a model mixture was added into a 50-mL volumetric flask filled with water for 2/3 of its volume. To create the desired pH value of ≈7.4, 5.0 mL of a 0.1 M solution of $NaHCO_3$ was added. One milliliter of a DSA solution and water to the mark were added, and the mixture was stirred thoroughly. All experiments were carried out at room temperature; exposure time (τ) was usually 10 min. In separate experiments, pH, the volume of the reagent solution, and the exposure time were alternately varied.

The absorption spectra of the solutions of azo dyes formed were recorded in 1 nm increments on an SF-2000 spectrophotometer in the range from 200 to 600 nm using 10.0-mm quartz cells. The absorbance of solutions (A) at the chosen value of λ was measured on a KFK-3-01 instrument. The reference solution was a blank solution or distilled water. The colored solutions were measured three times; the results of measurements were averaged. At $0.1 < A < 1.0$, the precision of repeated measurements was characterized by the values RSD < 2%. When the azo dye solution was again prepared, RSD < 3%; when the solution containing a mixture of various azo dyes was repeatedly prepared, RSD < 5%.

The molar absorption coefficients of azo dyes (ε) were calculated by averaging the values obtained at different initial concentrations of the initial phenol. It was assumed that the Bouguer–Lambert–Beer law was satisfied, and the molar concentration of the azo dye formed was equal to the concentration of the investigated phenol. As the absorbance of the measured solution varied with time, the results of calculations were conditional values of ε, which were characteristic only of the selected exposure time and were lower than the true molar absorption coefficients of the same azo dyes. The calibration curves for individual phenols were plotted by 5–7 points, calculating equations $A_i = a_i + k_i c_i$ by the least- squares technique. When the reference solution was chosen properly, the coefficient a_i was usually statistically insignificant. The results of analysis of model mixtures were calculated by Eq. (1), where k_{ph} is sensitivity coefficient in the determination of the simplest phenol:

$$c^* = A_\Sigma / k_{ph}. \quad (1)$$

The errors of analysis in the absence of interfering substances (Z) were calculated by the equation

$$\delta c = \frac{c^* - c_\Sigma}{c_\Sigma} \times 100\%. \quad (2)$$

Additional errors arising in the presence of interfering substances (Z) were found by Eq. (3), where c_Z^* is the result of analysis in the presence of Z,

$$\delta c_Z = \frac{c_Z^* - c^*}{c_\Sigma} \times 100\%. \quad (3)$$

The errors in the analysis of a number of mixtures by the same procedure were generalized using the RMSEP parameter [18]. The statistical processing of the data was carried out according to the traditional algorithm, assuming a normal distribution of random

errors ($n = 3$, $P = 0.95$). The relative value of deviations from the additivity of absorbances (ΔA_{rel}) at the chosen analytical wavelength (**AW**) was found by Eq. (4), and the significance of these deviations was checked using the 3*s*-test [19]

$$\Delta A_{rel} = \frac{A_\Sigma - \sum A_i}{\sum A_i} \times 100\%. \quad (4)$$

The intra-group selectivity of the analytical signals was evaluated using the parameter T equal to the ratio of the maximum and minimum sensitivity coefficients in measuring signals from the same type of analytes under identical conditions [5, 7]. In calculating the parameter T, the presence of *p*-nitrophenol, which virtually did not react with DSA, was not taken into account. The interval estimates c_Σ were obtained taking into account the possible systematic errors due to intra-group selectivity. At that, Eq. (5), derived in [20], was used

$$c^*(1+T)/2T \le c_\Sigma \le c^*(1+T)/2. \quad (5)$$

In order to test the new procedure, samples of sewage waters from an oil refinery, which were cleaned first, but not passed through the settling tanks of treatment facilities, were sampled and analyzed. Sampling was carried out as indicated in the procedure [9]. The analysis of the samples using the new procedure was carried out within 24 h after sampling.

RESULTS AND DISCUSSION

Absorption spectra of azo dyes. All of the phenols studied, except *p*-nitrophenol, react with DSA and give products (azo dyes) absorbing in the near UV and visible spectral regions. The reaction with DSA is more universal than the selective interaction of phenols with 4-AA. However, the absorbances of various azo dyes at a fixed wavelength, one and the same value of τ, and the same initial concentration of the initial phenols differed significantly (intra-group selectivity of the signals).

The absorption spectra of the products of phenol interaction with DSA are shown in Fig. 1. In the region 220–300 nm, there is strong absorbance of the reference solution due to the presence of DSA; here azo dyes almost do not absorb. In the region 300–450 nm, all azo dyes absorb. The background absorption of the excess of DSA is weak, but it cannot be neglected. The molar absorption coefficients of azo dyes at λ_{max} are 2×10^4–3×10^4 L/(mol cm) [16]. The sensitivity of the determination of azo dyes is somewhat inferior to the sensitivity of the determination of quinoneimine dyes, for which $\varepsilon \approx 3 \times 10^4$–$4 \times 10^4$ L/(mol cm) [15]. At $\lambda < 360$ nm, the derivatives of volatile phenols absorb more strongly than the derivatives of low-volatile phenols; at $\lambda > 410$ nm, the opposite relationship is observed. Differences between the signals of various phenols are minimal at 360–410 nm; just in this wavelength region AW should be chosen to estimate c_Σ.

Selection of the exposure time. It is known that, at high concentrations of certain phenols, the equilibrium of the reaction with DSA is established only within 2–3 min after mixing the reagents [16]. In dilute solutions, analytical signals of most phenols formed within 10–20 min, and then gradually decreased (Fig. 2). *P*-cresol reacts with DSA more slowly than other phenols; the absorbance of the corresponding solutions achieves a plateau only after 90–120 min, depending on the initial concentration of *p*-cresol. The shape of absorption spectra of the azo dye formed was similar to that of the spectra of azo dyes obtained from other phenols, and was virtually independent of the exposure time.

To prolong the duration of exposure, waiting for the completion of signal formation for all phenols is inappropriate because of the instability of certain azo dyes. The gradual decrease in analytical signals may be due to either the interaction of previously formed azo dyes with an excess of DSA, or to their oxidation by air oxygen. Long exposures are also undesirable with purely applied reasons, so that from here $\tau = 10$ min was used, neglecting the incompleteness of the formation of some azo dyes. It was desirable to increase exposure time to 90 or 120 min in the cases when it was known that the samples under investigation contained a lot of *p*-cresol or other "inert" phenols. The total duration of analysis in such cases significantly increased.

Influence of concentration conditions. To assess the effect of pH on the sensitivity of the determination of phenols, solutions of azo dyes were obtained at various pH values under other constant conditions. The necessary pH was attained by adding dilute solutions of hydrochloric acid or sodium hydroxide (potentiometric control) dropwise. For all phenols under study, pH value in the range 7.2–7.6, which appeared to be optimal. In more acidic and more alkaline solutions, the signals of all phenols decreased reliably (Table 1). pH beyond the optimal range resulted in an increase in intragroup selectivity (an increase in the parameter T) [17]. The effect of pH on the signals of phenols can not be explained by the ionization of phenols: in the pH region studied, all phenols, with the exception of *p*-nitrophenol, were in the same unionized form. Taking into account the published data [15], one can suppose that a decrease in the signals of all phenols at $pH < 7.2$ is explained by a decrease in the rate of formation of azo dyes, they did not form in an acidic medium at all. The decrease in signals at $pH > 7.8$ may be explained by the accelerated decomposition of azo dyes [2, 16].

Variation of the excess of DSA in the range 25–150 μM had no significant effect on phenol sig-

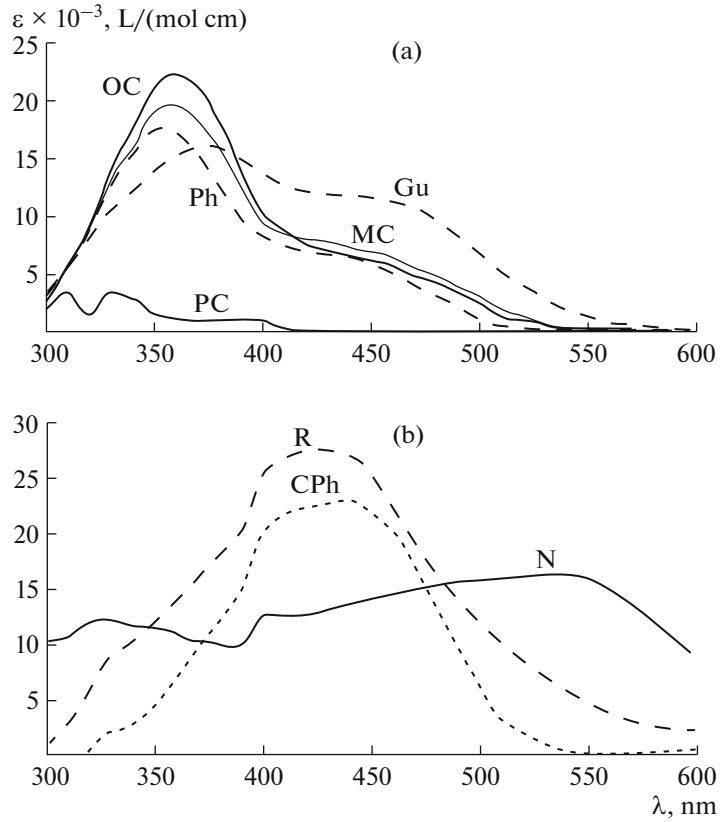


Fig. 1. Absorption spectra of the products of interaction of various phenols with DSA. (a) Derivatives of volatile phenols, (b) derivatives of low-volatile phenols. c_{DSA} = 100 μM, τ = 10 min, and the reference solution is the blank experiment solution.

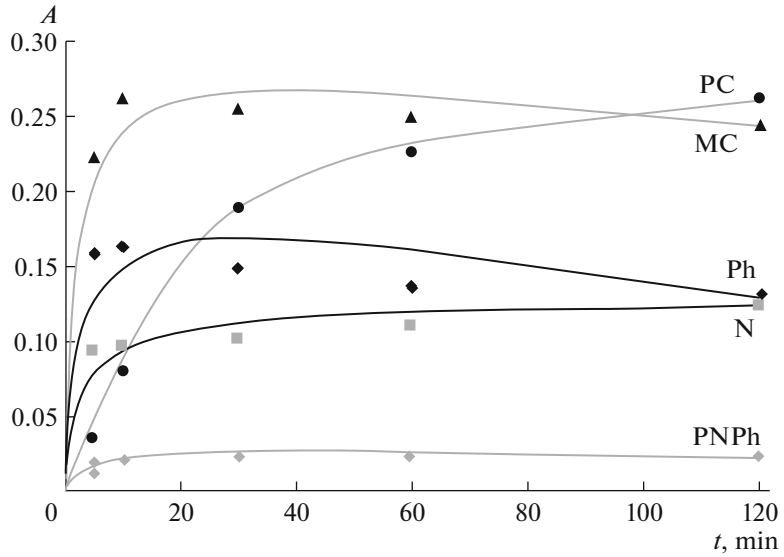


Fig. 2. Changes in analytical signals of some phenols in time. c_i = 10 μM, c_{DSA} = 100 μM, and λ = 380 nm.

nals. This explains the good reproducibility of the signals obtained using a low-stability reagent.

Calibration dependencies and choice of analytical wavelength. After the transfer of phenols into azo dyes, linear calibration curves were obtained for all model compounds in the concentration range from 1 to 20 μM at three AW (360, 380, and 410 nm). The coefficients of linear correlation in all cases exceeded 0.99; the lower limit of analytical range (LLAR) was close to 2 μM. The Cochran test showed that the convergence of the analytical signals was approximately the same in the determination of various phenols and with the use of various AW (the significance level of the null hypothesis was $\alpha < 0.05$). Obviously, when choosing AW, the convergence of the measurements can be ignored.

The limits of detection for individual phenols (c_{min}) after their transfer to azo dyes were calculated in a traditional way (according to Kaiser). Measurement of signals of phenols at the absorbance maxima of the corresponding azo dyes resulted in the values of c_{min} in the range of 0.1–0.4 μM. If we determine all phenols at 360 or 380 nm and express their concentrations in terms of the simplest phenol, the values of c_{min} slightly increase, but do not exceed 0.5 μM. Thus, when choosing the AW, the values of the detection limits may be ignored.

When choosing an AW, one should be guided by the level of intra-group selectivity of the signals. One-dimensional graduations, constructed for various phenols with the same AW, significantly differ in slope (Fig. 3). Thus, at $\lambda = 380$ nm and $\tau = 10$ min, the conditional molar absorption coefficients of azo dyes formed from various phenols after multiplying by 10^{-3} were: MC, 21.0; R, 20.9; OC, 18.2; Ph, 14.2; CPh, 14.0; N, 13.7; and Gu, 13.0 L/(mol cm). The parameter T for this sample of phenols is 1.6. The fan of calibrations at 360 nm is somewhat wider ($T = 2.3$), and at 410 nm T reaches 3.1. For comparison, when using 4-AA, the T parameter is about 5 units [5], without taking into account those phenols that do not react at all with 4-AA.

Table 1. Effect of pH on the analytical signals ($A \times 10^3$) of some phenols ($\lambda = 380$ nm, $\tau = 10$ min, and $c_i = 10$ μM)

pH	Phenol	Naphthol	*meta*-Cresol
7.0	131 ± 5	70 ± 5	167 ± 5
7.2	163 ± 3	88 ± 3	181 ± 3
7.4	164 ± 5	88 ± 2	182 ± 3
7.6	162 ± 2	87 ± 4	179 ± 2
7.8	160 ± 2	69 ± 3	167 ± 2
8.0	123 ± 7	32 ± 5	119 ± 4

Obviously, after carrying out a photometric reaction with DSA, a generalized analytical signal of the phenols is desirable to be measured at 380 nm, when the intra-group selectivity of the signals is minimal. Regardless of the total concentration of the phenols in the test sample, such choice should result in a more correct estimate of c_Σ [7], which was confirmed during the analysis of model mixtures. Total analytic signals of phenols can be measured also at 360 nm, since the calibration curve of the standard substance (the simplest phenol) in this case is in the middle of the graduation fan, which also contributes to the correct evaluation of c_Σ (at 380 nm, the relative arrangement of various graduations is less favorable). It is not recommended to measure phenol signals at 410 nm due to both high intra-group selectivity, and the low sensitivity of the determination of the standard substance (the simplest phenol).

Errors in the analysis of model mixtures. In Table 2 the data on the composition and results of analysis of some aqueous solutions simultaneously containing 2–3 phenols are presented. In total, more than 30 model mixtures were analyzed, for which the value of c_Σ in the final dilution was from 5 to 50 μM. Such mixtures may be considered as imitates of heavily polluted natural or treated wastewater. The results of the

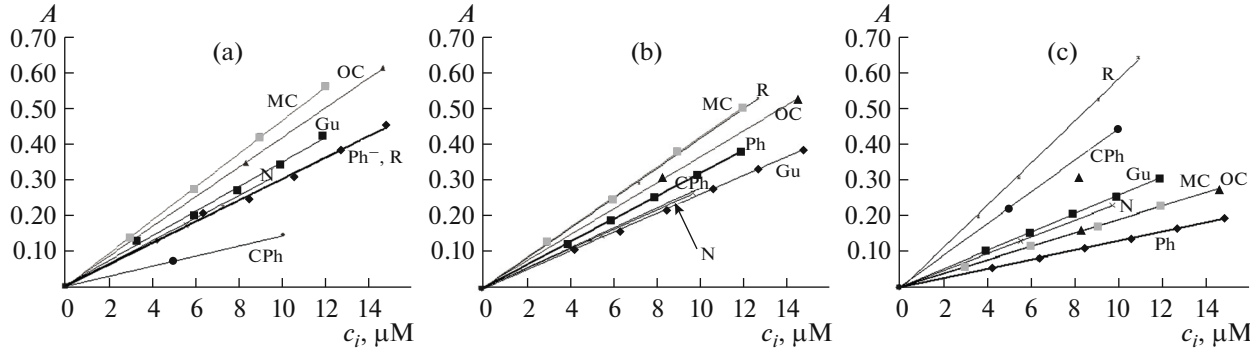


Fig. 3. Fans of calibration graphs in the determination of individual phenols by the reaction with DSA at three analytical wavelengths. $c_{DSA} = 100$ μM, $\tau = 10$ min, (a) 360 nm, (b) 380 nm, and (c) 410 nm.

Table 2. Results (c^*) and errors (δc, %) of the determination of the sum concentration of phenols in multicomponent aqueous solutions (mixtures) in the absence of interfering substances ($\lambda = 380$ nm, $\tau = 10$ min, standard substance is C_6H_5OH, and RMSEP = 1.8 μM)

Mixture number	Concentration of components, μM				Added, c_Σ, μM	Found, c^*, μM	δc, %	Interval estimation c_Σ, μM
	Ph	N	R	CPh				
1	–	7.0	3.7	–	10.7	8.8 ± 0.4	−18	7.1–11.4
2	10.7	–	5.5	–	16.2	17.3 ± 0.2	7	14.1–22.5
3	6.4	4.2	5.6	–	16.2	13.4 ± 0.3	−17	10.9–17.4
4	10.7	5.6	–	–	16.3	12.5 ± 0.3	−23	10.0–16.3
5	–	–	7.5	12.4	19.9	19.1 ± 0.4	−4	15.5–24.8
6	8.6	–	–	12.4	21.0	23.5 ± 0.2	12	19.1–30.6
7	6.4	–	5.6	9.3	21.3	20.3 ± 0.3	−5	16.5–26.4

analysis in all cases were expressed in terms of the simplest phenol. The errors in estimating the total phenol concentration at 380 nm were well reproducible, differed in sign, and did not exceed 30% modulo. The errors in estimating c_Σ at 360 nm were somewhat higher, and at 410 nm they often exceeded 50% level. The error characteristics (RMSEP values) at 360, 380, and 410 nm, which were generalized for all mixtures, were respectively 14, 10, and 20% of the average phenol concentration in the analyzed mixtures, which confirms the correctness of the choice of AW.

Since the coefficients of variation in the repeated measurement of generalized analytical signals do not exceed 5 rel. %, and the total phenol concentration is determined with much greater errors, the main contribution to the overall error in estimating c_Σ is made by systematic errors.

According to [5], analysis of multicomponent solutions of a known composition using 4-AA usually results in much more systematic errors (up to 80%), the results of the analysis being always underestimated. Thus, the transition to the azo coupling reaction and the optimization of measurements of the generalized signal make it possible to estimate the total phenol concentration more correctly than using 4-AA, without significant penalties of other characteristics (LLAR, precision, and duration of analysis).

Interval estimates of the total concentration of phenols. The results of the analysis of phenolic mixtures with the use of DSA may be represented in the interval form taking into account the expected systematic errors [20]. Since the sensitivity of determining the standard substance approximately corresponds to the middle of the graduation fan, the boundaries of these intervals may be calculated from the Eq. (5). The results of the calculations are given in Table 2 (last column). The corresponding intervals are much wider than the traditionally calculated confidence intervals, which take into account only the random errors in the measurements. One can see that the actual value of c_Σ in all cases falls within the limits of the found interval estimates. This indicates the main source of systematic analysis errors. Equation (5) is satisfied only when such a source is the discrepancy of the sensitivity coefficients when measuring signals of a standard substance and other analytes at the chosen AW [20]. One can also come to the same conclusion by looking at the signs of errors. Thus, the results of the analysis of mixtures containing *o*- and *m*-cresol were usually overestimated, and the results of the analysis of mixtures containing naphthol were underestimated (see data on mixtures 1, 3, and 4 in Table 2). It is nothing to be surprised about, since at 380 nm, *o*- and *m*-cresol are determined with higher sensitivity than the standard substance, and naphthol – with a smaller one. However, it is not possible to predict the magnitude of the systematic errors using the algorithm [21] when determining the phenols with DSA, sometimes even the error sign is incorrectly predicted. This indicates the presence of additional sources of errors, except for the intra-group selectivity of the signals.

Checking the additivity of absorbance of model mixtures. One of the sources of the systematic error in estimating the total concentrations may be nonadditivity of total signals. Thus, deviations from additivity strongly distort the results of the analysis of mixtures of polyphenolic antioxidants using the FRAP method [19], although they can be eliminated by increasing the excess of the photometric reagent.

We tested the additivity of the absorbance of phenols after their transfer to azo dyes by measuring the absorbance of mixtures and comparing it with the arithmetic sum of absorbances of components taken separately (Table 3). The corresponding phenolic mixtures are similar in their composition to the mixtures described in Table 2; each mixture contained from 2 to 5 individual phenols in various concentration ratios at the total phenol concentration from 10 to 30 μM. For most of the studied mixtures, deviations from additivity (ΔA) turned out to be negative in sign and small in absolute value (up to 10%). In some cases, the deviations were statistically significant. We

Table 3. Testing the additivity of analytical signals ($\lambda = 360$ nm, $\tau = 10$ min, standard substance is C_6H_5OH)

Mixture number	ΣA_i	A_Σ	ΔA*	$3s_{A\Sigma}$	Significance ΔA	δA, %
1a	0.134	0.120	−0.014	0.006	+	−10
2a	0.265	0.243	−0.022	0.013	+	−8
3a	0.189	0.185	−0.004	0.004	−	−2
4a	0.293	0.294	0.001	0.014	−	+0.3
5a	0.358	0.337	−0.021	0.011	+	−6
6a	0.311	0.300	−0.011	0.003	+	−4
7a	0.305	0.305	0.000	0.008	−	0
8a	0.203	0.202	−0.001	0.003	−	−0.5

* The deviation $\Delta A = A_\Sigma - \Sigma A_i$ is significant, if $|\Delta A| > 3s_{A\Sigma}$.

supposed that the observed deviations from additivity were caused, as in the case of antioxidants, by the lack of a photometric reagent [19]. However, an increase in the excess of DSA did not result in the elimination of the revealed deviations from additivity. We believe that they may be due to the formation of associates including various phenols. This should hinder the azo coupling reaction and result in the underestimation of the analysis results. Naturally, to accept or reject this hypothesis, more research is needed.

Influence of foreign substances. In determining total phenols in real samples, the influence of foreign substances (Z) may become an additional source of a systematic error. For checking purposes, substances that could react with phenols, DSA, or azo dyes were selected. Substance Z was introduced approximately in an equimolar amount relative to the preintroduced phenol, and then DSA was added and measurements were made. If the Z effect could not be detected, a 50 or 100-fold excess of Z was injected and a check was repeated. The resulting additional error was calculated by Eq. (3). It was found that the analytical signals of phenols were not affected by the ionic strength of the solution (in the test, KCl and other salts not affecting the pH of the solution were introduced). The determination of phenols is not affected by organic substances that knowingly do not react with phenols and DSA, in particular ethanol, glucose, and EDTA. There was also no effect of oxidizing agents (e.g., sodium chromate), although theoretically they could react with both phenols and DSA.

The result of the determination of phenols was reliably affected by reducing agents. In particular, sodium sulphite reduces the intensity of the absorbance of azo dyes, even when equimolar amounts are introduced. A hundredfold excess of sulfite ions almost completely suppressed the formation of azo dyes. This may be explained by the proceeding of a competing redox reaction between DSA and sulfite ions [22]. It should be noted that the detected effect may prevent the use of DSA in the analysis of waste water from pulp and paper plants, in which phenols (in particular, guaiacol) and sulphite liquors are always present [23].

Feigle showed that the determination of phenols with DSA is affected by aniline and other arylamines [24] and that they are even more active than phenols. According to our data, in the presence of equimolar amounts of arylamines, analytic signals of phenols were overestimated by 40–50%. The influence of alkylamines was much weaker. In particular, equimolar amounts of methylamine increased phenol signals by 10–20%.

Approbation of the procedure in the analysis of waste water. The proposed procedure for the determination of the total concentration of phenols in waters includes the following operations. One takes 40 mL of test water, adds $NaHCO_3$ to pH 7.4, and injects 1–2 mL of a 0.005 M DSA solution and distilled water to the mark (50.0 mL). After 10 min, the resulting solution is measured at 380 nm against the solution obtained in the blank experiment. Since the waste water sample may contain non-phenolic compounds absorbing in the UV region of the spectrum (e.g., light arenas), the absorbance of a sample solution without DSA was additionally measured, and, after the measurement of A_Σ, an appropriate correction was introduced. The value of c_Σ of the measured solution was found in terms of the simplest phenol from the previously constructed calibration curve. The total concentration of phenols in waste water (c_x, mg/L) was determined by taking into account the dilution of the sample and the molar mass of the standard substance. The duration of analysis of a single sample was about 30 min without taking into account the construction of a calibration curve.

According to the proposed procedure, several samples of purified sewage waters of an oil refinery were analyzed. The proportion of *p*-cresol in waters of this type is small [25]; therefore, a 10-min exposure is sufficient to form a total analytical signal. The values of PI of these samples, found by the standard procedure [9] in the factory laboratory, were in the range

30–50 μg/L. The values of c_x obtained by our procedure were 1.5–2 times higher than these values.

We consider the results of the determination of c_x only as a confirmation of the applicability of the new procedure in the analysis of hydrochemical samples. To confirm the accuracy of the results obtained, additional studies are required, using samples of various types and reference methods of analysis.

CONCLUSIONS

The study performed confirmed a possibility of a spectrophotometric evaluation of the sum concentration of phenols as azo dyes. As was already noted, in the analysis of aqueous solutions according to the proposed procedure, the value of LLAR in terms of the simplest phenol was close to 2 μM (~0.2 mg/L). This is 1–2 orders of magnitude higher than the values of the maximum permissible concentration of individual phenols in domestic waters [1] accepted in the Russian Federation [1]; therefore, it will be possible to apply a new procedure in the analysis of natural waters only after the preconcentration of phenols (distillation, extraction, sorption, etc.) or the azo dyes formed therefrom. The same restriction is also characteristic of the known procedures for the determination of phenols with 4-aminoantipyrine [4]. In the analysis of waste waters, both procedures may be used without preconcentration, because, in these waters, the concentration of phenol is significantly higher. In particular, both procedures ensure the estimation of the total concentration of phenols in waste waters of oil refineries. An advantage of the proposed procedure is that phenols that do not react with 4-aminoantipyrine, e.g., *p*-cresol, also enter into the reaction with DSA. However, such compounds react rather slowly with DSA. Another advantage is a lower level of intra-group selectivity. A targeted selection of AW and an increase in exposure time can further equalize the analytical signals of various phenols. According to our data, the systematic error in determining the sum concentration of phenols in aqueous solutions using DSA does not exceed 30% (at a concentration level of 10–30 μM). This is several times lower than in using 4-AA. Naturally, the error in the results of analysis of real hydrochemical samples may be above 30%, in particular, because of the interaction of DSA with reducing agents and/or arylamines; however, they also react with 4-AA. The disadvantages of the proposed procedure are certain small deviations from the additivity of analytical signals and a gradual decrease in the signals of some phenols in time, starting from the 20th min after the introduction of the reagent. The results of analysis may be underestimated if phenols that do not react with DSA, e.g. *para*-nitrophenol, are present in the water under study. The latter disadvantage is typical for all methods of the determination of the sum concentration of substances of a certain type, including their transfer to colored compounds under the influence of a "group reagent", the procedure for determining total phenols with DSA being more universal than the standard procedure based on the use of 4-AA. A decrease in the intragroup selectivity of the analysis in the transition from 4-AA to DSA ensures the more precise characterization of the sum concentration of phenols by interval estimations. To further reduce the uncertainty of such estimates, multiwave measurements can be used, as it was done in the spectrometric determination of the total concentration of hydrocarbons in waste waters [26].

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 16-43-550479, 2017, and the administration of the Omsk oblast. We are grateful to T.V. Antonova for the participation in the discussion of the plan and results of the work. Part of data was obtained with the participation of Yu.I. Vidimkina.

REFERENCES

1. Vorob'eva, T.V., Terletskaya, A.V., and Kushchevskaya, N.F., *Khim. Tekhnol. Vody*, 2007, vol. 29, no. 4, p. 370.
2. Korenman, I.M., *Fotometricheskii analiz. Metody opredeleniya organicheskikh soedinenii* (Photometric Analysis: Methods for the Determination of Organic Compounds), Moscow: Khimiya. 1975.
3. Magasumova, D.T., Khatmullina, R.M., Safarova, V.I., Kitaeva, I.M., and Kydasheva, F.Kh., *J. Anal. Chem.*, 2014, vol. 69, no. 3, p. 237.
4. Tropynina, L.V., Kartashova, A.V., Zhilina, I.V., Romanov, P.V., *Kontrol' Kachestva Produktsii*, 2012, no. 12, p. 27.
5. Antonova, T.V., Vershinin, V.I., Ivanova, V.A., and Shiligin, P.V., *Analitika Kontrol'*, 2012, vol. 16, no. 4, p. 343.
6. Goerlitz, D.F. and Brown, E., *Methods for Analysis of Organic Substances in Water*, Washington, DC: US Geol. Survey, 1984.
7. Vershinin, V.I., *Opredelenie summarnogo soderzhaniya odnotipnykh organicheskikh veshchestv (teoriya integral'nykh pokazatelei)* (Determination of the Total Concentration of the Same Type of Organic Substances (Theory of total indices)), Omsk: Omsk Gos. Univ., 2016.
8. Norwitz, G., Nataro, N., and Keliher, P.N., *Anal. Chem.*, 1986, vol. 58, no. 3, p. 639.
9. *RD* (Regulation Documentation) *52.24.488-2006: Mass Concentration of Volatile Phenols in Water. The Procedure for Performing Measurements by Extraction-Photometric Method after Steam Distillation*, Rostov-on-Don, 2006.
10. *RD* (Regulation Documentation) *52.24.480-2006: Mass Concentration of Volatile Phenols in Water. Method of Performing Measurements by Accelerated Extraction-Photometric Method without Distillation*, Rostov-on-Don, 2006.

11. *ISO 6439:1990: Water Quality. Determination of Phenol Index. 4-Aminoantipyrine Spectrometric Methods after Distillation*, 1990.
12. Khatmullina, R.M., Magasumova, D.T., and Safarova, V.I., *Bashkir. Khim. Zh.*, 2008, vol. 15, no. 3, p.48.
13. Vershinin, V.I., Safarova, V.I., Antonova, T.V., and Khatmullina, R.M., *Metody Otsenki Sootvetstviya*, 2013, no. 8, p. 22.
14. Sursyakova, V.V., Burmakina, G.V., and Rubailo, A.I., *Zh. Sib. Fed. Univ., Khim.*, 2010, vol. 3, no. 3, p. 268.
15. Whitlock, L.R., Siggia, S., and Smola, J.E., *Anal. Chem.*, 1972, vol. 44, no. 3, p. 532.
16. Siggia, S. and Hanna, J.G., *Quantitative Organic Analysis via Functional Groups*, New York: Wiley, 1980, 4 ed.
17. Antonova, T.V., Vershinin, V.I., and Vidimkina, Yu.V., RF Patent 25533322, *Byull. Izobret.*, 2014, no. 32.
18. Esbensen, K.H., *Multivariate Data Analysis — In Practice*, Oslo: CAMO, 2004.
19. Vershinin, V.I., Tsyupko, T.G., and Vlasova, I.V., *Metody Ob"ekty Khim. Anal.*, 2010, vol. 5, no. 4, p. 226.
20. Vershinin, V.I., Isachenko, N.A., and Brilenok, N.S., *J. Anal. Chem.*, 2016, vol. 71, no. 4, p. 351.
21. Vershinin, V.I., Tsyupko, T.G. and Brilenok, N.S., *J. Anal. Chem.*, 2012, vol. 67, no. 7, p. 649.
22. Shabarov, Yu.S., *Organicheskaya khimiya* (Organic Chemistry), Moscow: Khimiya, 2000.
23. Bogolitsyn, K.G., Soboleva, T.V., Gusakova, M.A., Pochtovalova, A.S., and Lichutina, T.F., *Nauchnye osnovy ekologo-analiticheskogo kontrolya promyshlennykh stochnykh vod TsBP* (Scientific Foundations of Ecological and Analytical Control of Industrial Wastewater of Pulp and Paper Industry), Ekaterinburg: Ural. Otd. Ross. Akad. Nauk, 2010.
24. Feigl, F., *Spot Tests in Organic Analysis*, New York: Elsevier, 1960, 6th ed.
25. Korenman, Ya.I. and Fokin, V.N., *Khim. Tekhnol. Vody*, 1993, vol. 15, nos. 7–8, p. 531.
26. Vershinin, V.I. and Petrov, S.V., *Talanta*, 2016, vol. 148, p. 163.

Translated by V. Kudrinskaya