DETERMINATION OF NON-VOLATILE PHENOLS IN WASTE WATERS OF OIL SHALE PROCESSING ENTERPRISES

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The cobaltnitrosoalkylresorcinolate method enables a selective determination of the total content of resorcinol series phenols ΣC_R in waste water of oil shale processing enterprises containing both mono- and dihydric phenols. The absorbance of phenol-containing solutions is measured at two combinations of $NaNO_2$ concentration and wavelength - E(I) and E(II). $\Sigma C_R = = pE(I) - qE(II)$. Five combinations of standard compounds used for the determination of coefficients p and q are evaluated. Analytical instruction is presented.

The new colorimetric method for the determination of resorcinol series phenols as cobaltnitrosoalkylresorcinolates is described in our previous paper [1]. Since coloured nitrosocobalt complexes are formed only with ligands containing nitroso groups in *ortho*-position to hydroxyl, this method for the determination of non-volatile phenols is more selective than other traditional colorimetric methods. Such a disposition is typical of nitrosation products of resorcinol series phenols only.

Volatile (hydroxybenzene series) phenols give *para*-nitrosated products and do not interfere. Oils, resins, oxidants and other compounds present in waste water do not react under the conditions of the analysis, and their interfering effect is negligible. The method is very sensitive: the sensitivity coefficient (the slope B_i of the calibration curve of the compound *i*) for the main representatives of resorcinolic pollutants in oil shale processing retort water varies between 0.344-0.975 dm³/mg when measured in 5 cm cells.

The absorbance (E) of the solution under study depends, besides the total content of resorcinol series phenols (ΣC_R), on the composition of the mixture, because B_i of individual compounds may differ up to 2.8 times. The same occurs when traditional reagents for phenols - 4-amino-

antipyrine and 4-nitroaniline - are used [2]. The latter case is even more complicated because volatile phenols also give coloured products when interact with these reagents. Furthermore, using traditional methods the differences between B_i are considerably greater than those of the new method depending essentially on the wavelength of measurements.

The determination of ΣC_R using the cobaltnitrosoalkylresorcinolate method would be perfect if the standard for the determination of the calibration curve contained individual compounds i in the same proportion as the tested solution. Then

$$\Sigma C_R = E/\overline{B}_i \qquad (1)$$

However, the estimation of the share of individual components in numerous mixtures under study is extremely laborious and would nullify the advantage of this simple method.

In the present paper we demonstrate that the total content of non-volatile phenols present in oil shale processing plant waste waters can be satisfactorily measured by colorimetry using the cobaltnitrosoresorcinolate method even when the component composition of phenols is unknown. The general idea of using this method bases on the fact that the main representatives of resorcinol series phenols in oil shale retort water may be divided, according to their sensitivity coefficients, into two distinct groups:
(1) phenols forming dinitroso derivatives: resorcinol, 4- and 5-alkylresorcinols;
(2) phenols forming mononitroso derivatives: 2-alkyl- and dialkylresorcinols.*

The absorbance of water solutions containing phenols of both groups was measured:
(1) at the maximum values of the average sensitivity coefficients of both groups, and
(2) at the maximum difference between the average sensitivity coefficients of both groups. Denoting the total concentration of both groups ΣC_{i1} and ΣC_{i2}, and the corresponding values of measured absorbances E (I) and E (II), the following system of equations may be presented

$$E \text{ (I)} = \overline{B}_{i1}(\text{I}) \, \Sigma C_{i1} + \overline{B}_{i2}(\text{I}) \, \Sigma C_{i2}; \qquad (2)$$

$$E \text{ (II)} = \overline{B}_{i1}(\text{II}) \, \Sigma C_{i1} + \overline{B}_{i2}(\text{II}) \, \Sigma C_{i2}; \qquad (3)$$

$$\Sigma C_R = \Sigma C_{i1} + \Sigma C_{i2} \qquad (4)$$

where $\overline{B}_i$ is the average sensitivity coefficient of the group;
        indices 1 and 2 denoting the group;
        (I) and (II)   are the conditions of the measurement.

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*In principle, trialkylresorcinols belong also to this group, but their sensitivity coefficients are smaller than those of other phenols of this group. Trialkylresorcinols constitute only up to 5 % of the total content of water-soluble phenols. As a rule, their share in the waste water phenols is below 1-2 %. Disregard of these compounds results in no pronounced error.

Table 1. Individual (B_i) and Partial (b_i) Sensitivity Coefficients (dm³/mg) of Resorcinol Series Phenols at Combinations I and II

Compound	% of the total content*	% of the given group	B_i (I)	b_i (I)	B_i (II)	b_i (II)
Resorcinol (R)	3.2±0.2	7.1	0.975±0.016	0.0692	0.593±0.007	0.0421
4-Methylresorcinol (4-MR)	1.9±0.1	4.2	0.721±0.012	0.0303	0.482±0.005	0.0202
5-Methylresorcinol (5-MR)	29.8±1.2	66.1	0.847±0.003	0.5599	0.608±0.005	0.4019
5-Ethylresorcinol (5-ER)	10.2±0.6	22.6	0.828±0.013	0.1871	0.610±0.005	0.1379
$\overline{B}_{i1}$			0.843	0.846	0.573	0.602
2-Methylresorcinol (2-MR)	1.8±0.1	6.7	0.352±0.007	0.0236	0.139±0.002	0.0093
2,5-Dimethylresorcinol (2,5-DMR)	10.6±0.9	39.7	0.432±0.005	0.1715	0.107±0.003	0.0425
4,5-Dimethylresorcinol (4,5-DMR)	9.2±0.4	34.5	0.344±0.011	0.1187	0.132±0.002	0.0455
2-Methyl-5-ethylresorcinol (2-M5ER)	5.1±0.4	19.1	0.376±0.003	0.0718	0.089±0.002	0.0171
$\overline{B}_{i2}$			0.376	0.386	0.117	0.114

* Monohydric phenols 10.8±1.3 %, other alkylresorcinols (AR, c. 50 compounds) 17.4±3.0 %.

Equations (2)-(4) give

$$\sum C_R = \frac{E(\text{I}) \ [\overline{B}_{i1}(\text{II}) - \overline{B}_{i2}(\text{II})] - E(\text{II}) \ [\overline{B}_{i1}(\text{I}) - \overline{B}_{i2}(\text{I})]}{\overline{B}_{i2}(\text{I}) \ \overline{B}_{i1}(\text{II}) - \overline{B}_{i1}(\text{II}) \ \overline{B}_{i2}(\text{II})} \qquad (5)$$

Experimental and Discussion

The same apparatus, standards and reagents as used for the analysis of individual phenolic compounds [1] were applied. By the results of our previous study, the following initial conditions were chosen for the first combination: the concentration of $CoSO_4$ and $NaNO_2$ - $1 \cdot 10^{-3}$ and $0.20 \ mol/dm^3$, respectively; pH - 4.5; the length of colorimetric cells - 5 cm, and wavelength (λ) of absorbance measurements - 420 nm. The second combination differed from the first one only in regard to the concentration of $NaNO_2$ ($0.05 \ mol/dm^3$) and λ (455 nm).

Under these two conditions the calibration curves for main individual phenolic compounds (i) present in oil shale retort water were obtained. In the concentration range studied, the curves may be approximated to straight lines. Their slopes B_i, and partial slopes b_i of curves corresponding to the average composition of industrial retort water tested by the authors, are given in Table 1.

Ten different phenol mixtures (Table 2) were analyzed to estimate the applicability of the method. The absorbancies of water solutions of their nitrosocobalt complexes at two combinations of conditions described above are presented in Table 3.

Table 2. **Composition of Phenols in Water Samples, mg/m³**

Compound	Number of mixture									
	1	2	3	4	5	6	7	8	9	10
Hydroxybenzene	10	100	65	25	200	125	50	400	17	1070
R	10	25	25	25	50	50	50	100	39	17
4-MR	6	15	15	15	30	30	30	60	51	76
5-MR	50	125	188	250	250	375	500	500	175	215
5-ER	50	25	25	25	50	50	50	100	-	-
2-MR	2	20	12.5	5	40	25	10	80	31	150
2,5-DMR	20	25	37.5	50	50	75	100	100	199	295
4,5-DMR	20	25	37	50	50	75	100	100	6	5
2-M5ER	10	25	25	25	50	50	50	100	39	2
2-E5MR	10	25	25	25	50	50	50	100	50	70
Other AR	-	-	-	-	-	-	-	-	60	100
Total	188	410	455	495	820	905	990	1640	667	2000
Including:										
ΣC_{i1}	116	190	253	315	380	505	630	760	265	308
ΣC_{i2}	62	120	137	155	240	275	310	480	385	622

Table 3. **Absorbance of Nitrosocobalt Complex in Water**

Number of mixture (see Table 2)	ΣC_R, mg/dm^3	E (I)	E (II)
1	0.178	0.144	0.096
2	0.310	0.203	0.128
3	0.390	0.260	0.163
4	0.470	0.326	0.195
5	0.620	0.389	0.226
6	0.780	0.495	0.292
7	0.940	0.617	0.363
8	1.240	0.739	0.421
9	0.650	0.352	0.173
10	0.930	0.360	0.103

For calculating ΣC_R according to Eq. (5), the values of absorbances E (I) and E (II) as well as the average sensitivity coefficients of both groups $\overline{B}_{i1}$ and $\overline{B}_{i2}$ are needed. It is unfeasible to determine the latters for every tested mixture; one has to use approximations satisfying the accuracy of technical analysis.

Let us examine the difference between the actual and calculated values of ΣC_R when the following average values of sensitivity coefficients are used instead of the B_i values of each sample:

• arithmetical mean of B_i of main components of both groups (case 1);

• average corresponding to the average composition of retort waters analyzed (case 2);

• sensitivity coefficients B_k and B_l of two phenols k and l found to be the most suitable representatives for both groups of phenols (case 3).

The latter case is certainly most suitable for practical application whereas the possibility to use 5-methylresorcinol and 2,5-dimethylresorcinol as the most easily available standards (case 3-1) is of a special interest.

Let us simplify Eq. (5) introducing the coefficients p and q

$$\frac{\overline{B}_{i1}(\text{II}) - \overline{B}_{i2}(\text{II})}{\overline{B}_{i2}(\text{I})\ \overline{B}_{i1}(\text{II}) - \overline{B}_{i1}(\text{I})\ \overline{B}_{i2}(\text{II})} = p; \tag{6}$$

$$\frac{\overline{B}_{i1}(\text{I}) - \overline{B}_{i2}(\text{I})}{\overline{B}_{i2}(\text{I})\ \overline{B}_{i1}(\text{II}) - \overline{B}_{i1}(\text{I})\ \overline{B}_{i2}(\text{II})} = q \tag{7}$$

whereas the general form of Eq. (5) may be expressed as

$$\Sigma C_R = pE\,(\text{I}) - qE\,(\text{II}) \tag{8}$$

The coefficients p and q obtain numerical values presented in Table 4 depending on the case chosen for calculation $\overline{B}_{i1}$ and $\overline{B}_{i2}$.

Table 4. **Coefficients p and q in Equation (8)**

| Case	Standard	$\overline{B}_{i1}$ and $\overline{B}_{i2}$	p	q
1	The mixture according to Table 1	$\overline{B}_{i1} = (\sum\limits_{i=1}^{n_1} B_{i1}) / n_1$ $\overline{B}_{i2} = (\sum\limits_{i=1}^{n_2} B_{i2}) / n_2$	3.77	3.80
2	As in **case 1**	$\overline{B}_{i1} = \sum\limits_{i=1}^{n_1} b_{i1}$ $\overline{B}_{i2} = \sum\limits_{i=1}^{n_2} b_{i2}$	3.58	3.34
3-1	$k = 5\text{-MR}$ $l = 2,5\text{-DMR}$	$\overline{B}_{i1} = B_k; \overline{B}_{i2} = B_l$	2.91	2.42
3-2	As in **case 3-1**	$\overline{B}_{i2}(\mathrm{I}) = 0.894 B_l(\mathrm{I})$; $\overline{B}_{i1}$ and $\overline{B}_{i2}(\mathrm{II})$ are the same as in **case 3-1**	3.48	3.20
3-3	$k = 5\text{-MR}$ $l = 2\text{-M5ER}$	$\overline{B}_{i1} = B_k; \overline{B}_{i2} = B_l$	3.39	3.08

The comparison of the actual ΣC_R for mixtures given in Table 2 with the values calculated on the basis of $E(\mathrm{I})$ and $E(\mathrm{II})$ for five different cases (Figure) demonstrates that the mean difference does not exceed 7 % irrespective of the method of approximation of $\overline{B}_{i1}$ and $\overline{B}_{i2}$. Moreover, except for the case 3-1 this number lies between 3.6-4.0 %.

It is remarkable that the actual and calculated values satisfactory coincide even when samples *9* and *10* were analyzed. These samples were prepared by solution of industrial tar-like phenol mixtures (previously analyzed by gas chromatography) [4, 5]. The actual and calculated values of ΣC_R coincide, as expected, even when besides resorcinol series phenols a remarkable amount of monohydric phenols was present (e.g. sample *10*, Table 2).

Table 5. **Parameters of the Regression Curve**
$Y = a + bX$. X - Actual Concentration, mg/dm^3;
Y - Found Concentration, mg/dm^3

Parameter	Case				
	1	2	3-1	3-2	3-3
a	-0.001	0.014	0.027	0.015	0.017
b	0.987	1.004	0.890	0.987	0.972
s_a	0.019	0.018	0.026	0.019	0.019
s_b	0.026	0.024	0.036	0.027	0.026
r	0.997	0.998	0.993	0.997	0.997
s	0.026	0.024	0.036	0.027	0.026

The parameters of curves describing the dependence between actual (X) and found (Y) concentrations (Table 5) attest that no calculation variant leads to an essential parallel shift between the results ($a < s_a$). Systematic error exceeds the accidental one only in case 3-1.
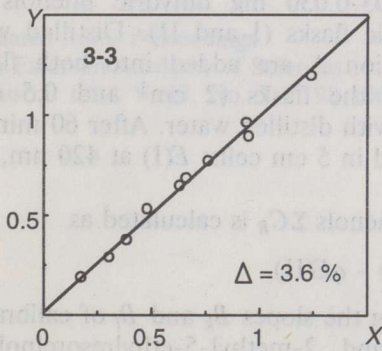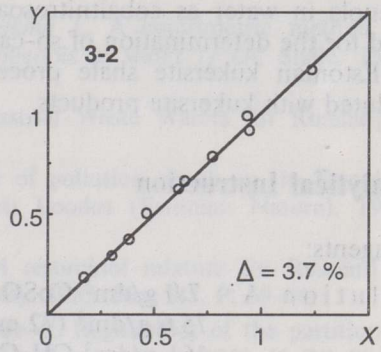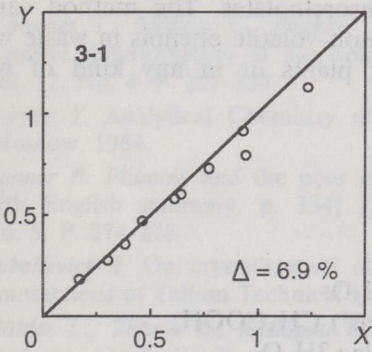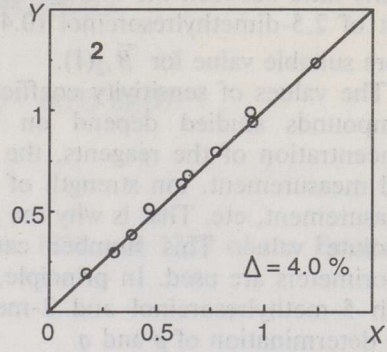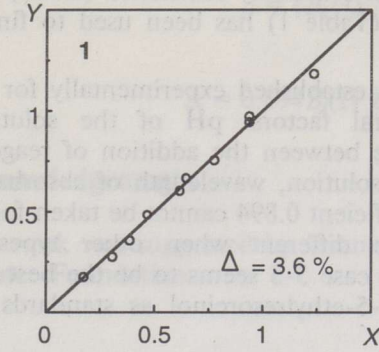
Found concentrations (Y, mg/dm³) versus actual (X, mg/dm³) ones. Numeration of figures denotes the calculation cases as given in Table 4

The difference between the actual and found concentrations in that case is caused by the fact that 2,5-dimethylresorcinol was used as the standard for determination of $\overline{B}_{i2}(I)$. The sensitivity coefficient for this compound is the highest in the second group of resorcinol derivatives (see Table 1). In case of 3-2, an improvement coefficient (0.894) corresponding to the ratio between the average weighed sensitivity coefficient (0.386) and that of 2,5-dimethylresorcinol (0.432) (Table 1) has been used to find a more suitable value for $\overline{B}_{i2}(I)$.

The values of sensitivity coefficients established experimentally for the compounds studied depend on several factors: pH of the solution, concentration of the reagents, the time between the addition of reagents and measurement, ion strength of the solution, wavelength of absorbance measurement, etc. That is why the coefficient 0.894 cannot be taken for an absolute value. This number can be different when other types of colorimeters are used. In principle, the case 3-3 seems to be the best one with 5-methylresorcinol and 2-methyl-5-ethylresorcinol as standards for the determination of p and q.

The results presented above form the basis for the new colorimetric method for the determination of the total content of resorcinol series phenols in water as cobaltnitrosoalkylresorcinolates. The method can be used for the determination of so-called non-volatile phenols in waste water of Estonian kukersite shale processing plants or in any kind of water polluted with kukersite products.

Analytical Instruction

Reagents:

Solution A: 7.0 g/dm³ $CoSO_4 \cdot 7H_2O$;
                    75.6 g/dm³ (72 cm³/dm³) CH_3COOH;
                    161 g/dm³ $CH_3COONa \cdot 3H_2O$.
Solution B: 172 g/dm³ $NaNO_2$.

Aliquots of water containing 0.003-0.030 mg dihydric phenols are transferred into two 25 cm³ volumetric flasks (I and II). Distilled water (up to 20 cm³) and 2 cm³ of solution A are added into both flasks. Thereafter solution B is added into the flasks (2 cm³ and 0.5 cm³, respectively), and the flasks are filled with distilled water. After 60 minutes the absorbance of solutions is measured in 5 cm cells: $E(I)$ at 420 nm, and $E(II)$ at 455 nm.

The total content of non-volatile phenols ΣC_R is calculated as

$$\Sigma C_R = pE(I) - qE(II).$$

Coefficients p and q are found using the slopes B_k and B_l of calibration curves for 5-methylresorcinol (k) and 2-methyl-5-ethylresorcinol (l) according to the Equations

$$p = [B_k(II) - B_l(II)]/\Delta;$$

$$q = [B_k(I) - B_l(I)]/\Delta$$

where (I) and (II) indicate the conditions of measurements, and

$$\Delta = [B_f(I) B_k(II) - B_k(I) B_f(II)].$$

Instead of 2-methyl-5-resorcinol, more available 2,5-dimethylresorcinol may be used as the standard l. Then

$$q = [B_k(I) - 0.894 B_f(I)]/\Delta,$$

and

$$\Delta = 0.894 B_f(I) B_k(II) - B_k(I) B_f(II).$$

Acknowledgements

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