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## A COLORIMETRIC METHOD FOR SELECTIVE DETERMINATION OF NON-VOLATILE PHENOLS IN WATER

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*A new selective colorimetric method for determination of resorcinol and its alkyl derivatives (1,3-benzenediols), the main phenolic pollutants in Estonia, has been elaborated. The overall reactions of the formation of cobalt-nitroso(alkyl)-resorcinolates according to this method are presented. The results of the experiments to find optimum values for pH and reagent concentrations as well as spectra of complexes formed from mono- and dialkyl derivatives of resorcinol are presented. Analytical instruction and parameters of calibration curves for main phenolic components in retort water of Baltic "kukersite" oil shale are given.*

### Introduction

The fact that phenolic compounds formed as a result of retorting of Baltic "kukersite" oil shale are mainly dihydric phenols, consisting of alkyl derivatives of 1,3-benzenediol (resorcinol), belongs to the specific characteristics of this oil shale.

Toxic properties of mono- and dihydric phenols differ essentially. Consequently, the effluent charges for waste disposal of these compounds should be differentiated, too. Paradoxically, up to now only monohydric (steam distillable) phenols have been determined for estimating phenolic pollution in Estonia. Hence over 80 % of phenolic compounds disposed have been completely ignored or classified as "total phenols" - a sum of mono- and dihydric phenols, an indefinite notion regarding environmental pollution.

There are two reasons for such a situation.

Firstly, environmental pollution caused by hydroxybenzene series phenols occurs around the world and therefore its effect on the surrounding nature has been studied in detail. Monohydric phenols are known as most hazardous compounds and an extremely severe concentration limit ( $10^{-4}$  mg/dm<sup>3</sup>) has been established for their content in water bodies. However, pollution caused by dihydric phenols, mainly

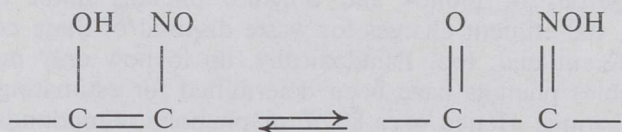
resorcinols of kukersite origin, is a specific problem of Estonia, little studied somewhere else. The information about occurrence, stability and environmental danger of resorcinol derivatives is incomplete. Their allowed concentration limits are established only in few countries, and they are 100-1000 times higher than those for hydroxybenzene derivatives.

Secondly, there is not known any simple and inexpensive method for the reliable determination of dihydric phenols in diluted solutions yet. All the reagents (4-aminoantipyrine, nitroaniline, amidopyrine, etc.) used at traditional colorimetric testing methods give a colour reaction with both mono- and dihydric phenols. The colour intensity of different compounds varies within a large range. Therefore the separate determination of mono- and dihydric phenols is possible only after separation of monohydric phenols from the background matrix by steam distillation. Besides, the results, especially concerning dihydric phenols, are interfered by oils, resins, several oxygen and sulphur compounds, aromatic amines, etc. present in water. The methods for avoiding the interference of these compounds are either quite lacking or they reduce the precision of analysis being at the same time laborious and reagent-consuming. The application of a sensitive high-pressure liquid chromatograph [1] will remain inaccessible for most of laboratories checking phenolic pollution in Estonia, for at least the nearest future. Such an apparatus is suitable for special studies rather than for a large number of samples.

The aim of this study was to create a new colorimetric method for the selective quantitative determination of individual resorcinol derivatives in waste water.

## Method

The new test method for dihydric phenols of resorcinol series in water is based on special structural properties of resorcinol alkyl derivatives: any electrophilic substitution reaction always occurs in *ortho*-position with respect to one of the two hydroxyl groups. Due to this, at nitrosation of resorcinol series phenols nitroso derivatives are formed which contain the group being subjected to tautomeric equilibrium



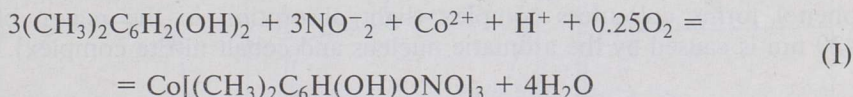
As a rule, these compounds are selective ligands for cobalt cation. At nitrosation of monohydric phenols, the reaction occurs preferably in *para*-position [2] and the reaction product does not form any complex with cobalt ion.

It is known that at nitrosation reaction in acidic aqueous solutions when the concentration of phenols approaches their saturation point, the following products are formed: resorcinol gives 2,4-dinitrosoresorcinol (DNR), 5-methylresorcinol (5-MR) gives 2,4-dinitroso-5-methylresorcinol (DNMR). However, 2,5-dimethylresorcinol (2,5-DMR) gives 4-nitroso-

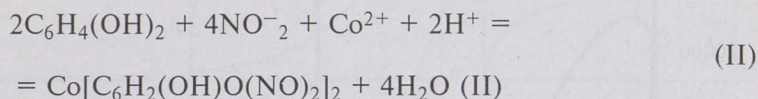


2,5-dimethylresorcinol (NDMR) [3]. For dinitroso derivatives, the constants  $pK_{a1}$  and  $pK_{a2}$  characterizing dissociation of *o*-hydroxynitroso groups are 4.66 and 7.9 for DNR, and 4.62 and 9.48 for DNMR, respectively. The value of  $pK_a$  for the mononitroso derivative NDMR is 3.46 [4]. Studies on the possibility of using NDMR for separation of cobalt from solutions have shown that in a weakly acidic solution a complex with the molar ratio NDMR:Co 3 : 1 and with the stability constant  $3.8 \cdot 10^{12}$   $(\text{mol}/\text{dm}^3)^{-3}$  [5] is formed. It is known that in analogous conditions DNR and cobalt form a precipitate with the molar ratio of components 2 : 1 [6]. There are no data published about complexes formed between DNMR and Co.

These facts enable us to describe the process occurring with the participation of 2,5-DMR and other dialkyl derivatives of resorcinol by the following equation



and in case of resorcinol and, probably, of its monoalkyl derivatives, by the equation



It is obvious that the testing of diluted samples of phenols (below  $10^{-4}$   $\text{mol}/\text{dm}^3$ ), typical for waste waters, requires a substantial excess of reagents to guarantee as complete as possible nitrosation of resorcinol derivatives and binding of cobalt complex. Unfortunately, there are no data published about nitrosation and complex formation under these conditions. Evidently, the concentration of any reagent must not be too high. An increase in the concentration of acid stimulates the nitrosation but simultaneously promotes the decomposition of nitrite and inhibits the formation of cobalt complex. An excess of nitrite may displace nitroso ligand in the complex. When the concentration of cobalt ions is extremely high, the optical density of the background increases.

Due to those circumstances, it is necessary to determine the optimum conditions of testing experimentally.

## Experimental

### *Reagents and Methods*

Resorcinol series phenols used in our experiments were synthesized at the Institute of Chemistry and at the Tallinn Technical University, or separated from oil shale originated phenols [7, 8]. The purity of these compounds was at least 98 %. In most experiments reagent grade 5-MR and 2,5-DMR as the most typical mono- and dialkyl derivatives of

resorcinol present in retort water of oil shale processing were employed. Cobalt sulphate and sodium nitrite were of analytical grade.

Optical density of the solutions was measured spectrophotometrically on "SPECOL 11", and acidity - on pH-meter "pH 262".

### Spectral Characterization

The dependence of molar extinction coefficients ( $\epsilon$ ) on wavelength for nitrosated phenol, 5-MR and 2,5-DMR in cobalt complexes was measured in solutions containing the phenolic component,  $\text{CoSO}_4$  and  $\text{NaNO}_2$  in quantities  $4 \cdot 10^{-5}$ ,  $1 \cdot 10^{-3}$  mol/dm<sup>3</sup>, and 0.2 mol/dm<sup>3</sup>, respectively. The value of pH was kept at 4.5 with the help of acetate buffer.

Figure 1 shows that at these conditions the cobalt complexes of 5-MR and 2,5-DMR nitroso derivatives are absorbing light intensively within the spectrum range 400-500 nm. On the other hand, nitrosated phenol forms colourless complex (light absorption in the region below 420 nm is caused by the aromatic nucleus and cobalt nitrite complex).

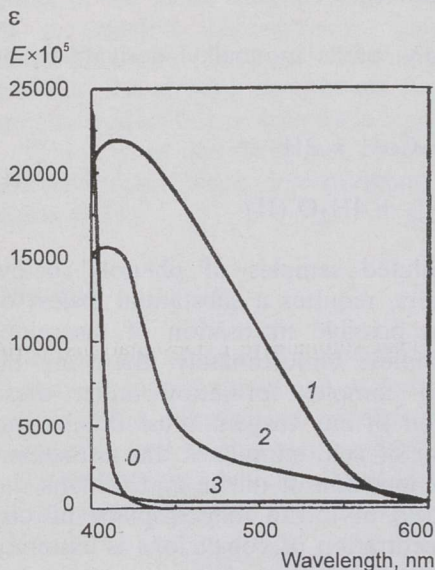


Fig. 1. Molar extinction coefficients ( $\epsilon$ , dm<sup>3</sup>/mol·cm) of nitrosated 5-MR (1), 2,5-DMR (2), and phenol (3) in cobalt complexes and absorbance ( $E$ ) of the reagent blank (0) in the visible region of spectrum

In the visible region of the spectrum, the absorbance of solutions  $E$  increases with decreasing wavelength. At wavelengths less than 560 nm, molar extinction coefficient of nitrosated 5-MR in cobalt complex essentially exceeds that of 2,5-DMR. The difference between the values of optical densities of a complex and the reagent blank is greatest at the region about 420 nm.

### Effect of pH

The formation of the cobalt complex occurs most completely in a weakly acidic solution. When the solution contains 1 mg resorcinol series phenol, 0.2 mol  $\text{NaNO}_2$  and  $1 \cdot 10^{-3}$  mol  $\text{CoSO}_4$  per dm<sup>3</sup>, the pH value between



3.5 and 5.5 is optimum for the complex formation (Fig. 2a). It can be explained by the fact that in more acidic solution, the complex formation is hindered both by nitrite decomposition and by a decrease in the amount of reactive anionic form of the nitroso compound. On the other hand, more basic solutions do not contain enough nitrosonium cations needed for nitrosation, and the complex formation is inhibited by hydrolysis of cobalt ions. When the concentration of the phenolic component or cobalt ions is increased, the optimum pH range enlarges towards more acidic solutions. The increase in  $\text{NaNO}_2$  concentration shifts this range to more neutral solutions.

The optimum pH may be maintained with the help of acetate buffer.

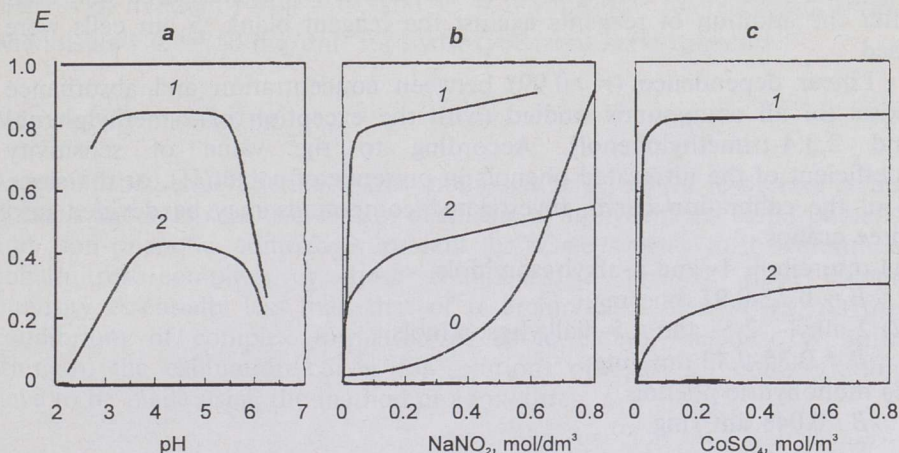


Fig. 2. Plot of absorbance of solutions of cobalt complexes versus pH (a), concentration of sodium nitrite (b) and cobalt sulphate (c). Designations of the curves are given in Fig. 1

### Concentration of Reagents

An excess of  $\text{CoSO}_4$  and  $\text{NaNO}_2$  is needed first of all for shifting the equilibrium of complex formation as right as possible. This excess must also guarantee a rate of complex formation exceeding the rate of the decomposition of nitrosating reactant  $\text{HNO}_2$  in a weakly acidic solution.

If pH is maintained at 4.5, the concentration of  $\text{NaNO}_2$  needed for nitrosation of 5-MR has to be at least  $0.05 \text{ mol/dm}^3$ , and for nitrosation of 2,5-DMR -  $0.2 \text{ mol/dm}^3$  (see Fig. 2b). At further elevation of  $\text{NaNO}_2$  concentration the absorbance of the background increases sharply due to the formation of a cobalt-nitrite complex. At  $\text{NaNO}_2$  concentration  $0.2 \text{ mol/dm}^3$ , optimum concentration of  $\text{CoSO}_4$  for monoalkyl derivatives is  $(1-2) \cdot 10^{-4}$  and for dialkyl derivatives -  $(5-10) \cdot 10^{-4} \text{ mol/dm}^3$  (Fig. 2c).

In order to obtain the maximum extinction coefficient, it is necessary to add at first cobalt sulphate and thereafter sodium nitrite to the test solution. This enables to avoid decomposition of the nitroso product before the formation of a stable cobalt complex.

### The Time Needed for Reaching the Equilibrium, and Colour Stability

Under optimum conditions of complex formation, the maximum absorbance of 5-MR and 2,5-DMR solutions is obtained after 20 and 60 min, respectively. The intensity of colour is stable (in the range of measurement error) for at least 6 hours.

### Sensitivity of the Method, Measurement Limits

Table presents parameters of calibration curves for most typical phenols present in waste waters. Measurements were done under optimum conditions (pH 4.5,  $\text{NaNO}_2$  0.2 mol/dm<sup>3</sup>,  $\text{CoSO}_4$   $1 \cdot 10^{-3}$  mol/dm<sup>3</sup>, wavelength 420 nm). Absorbance of the solutions was measured one hour after the addition of reagents against the reagent blank, 5 cm cells were used.

Linear dependence ( $r > 0.99$ ) between concentration and absorbance exists for all compounds studied (with the exception of 2-methylphenol and 2,3,4-trimethylphenol). According to the value of sensitivity coefficient of the nitrosated phenols in presence of cobalt(II), or the slope  $B$  of the calibration curve, investigated compounds may be divided into three groups:

- (1) resorcinol, 4- and 5-alkylresorcinols,  
 $B = 0.72\text{-}0.97 \text{ dm}^3/\text{mg}$ ;
- (2) 2-alkyl-, 2,5- and 4,5-dialkylresorcinols,  
 $B = 0.35\text{-}0.43 \text{ dm}^3/\text{mg}$ ;
- (3) monohydric phenols,  
 $B < 0.048 \text{ dm}^3/\text{mg}$ .

### Data of Calibration Curves

Component	$B$	$r$	$s_A$	$s_B$	$C_{99, \text{min}}, \text{mg}/\text{dm}^3$
Resorcinol	0.975	0.999	0.010	0.016	0.059
5-Methylresorcinol	0.847	0.999	0.002	0.003	0.029
5-Ethylresorcinol	0.828	0.999	0.008	0.013	0.060
4-Methylresorcinol	0.721	0.999	0.007	0.012	0.026
2-Methylresorcinol	0.352	0.998	0.005	0.007	0.076
2,5-Dimethylresorcinol	0.432	0.998	0.003	0.005	0.056
4,5-Dimethylresorcinol	0.344	0.996	0.007	0.011	0.110
2-Methyl-5-ethylresorcinol	0.376	0.999	0.002	0.003	0.030
Phenol	0.008	0.995	0.008	0.001	17
2,3-Dimethylphenol	0.046	0.995	0.011	0.002	7
2,6-Dimethylphenol	0.023	0.985	0.011	0.002	13
3,4-Dimethylphenol	0.048	0.994	0.005	0.008	6
2-Methylphenol	-0.001	0.099*	0.002	0.003	-
2,3,4-Trimethylphenol	0.007	0.439*	0.003	0.005	-

\* The linear dependence does not exist.

The precision data presented in the Table, demonstrate that the upper limit of the concentration of resorcinol series phenols varies between 1-3 mg/l (absorbance 1.0 at 420 nm, 5 cm cell). The dependence of absorbance on concentration remains linear within a very large range, even



in 50-100 times more concentrated solutions, if one uses a smaller size cell and a longer wavelength.

The lower limit of determination was established by a well-known equation [9]:

$$C_{\min} = (t_{P,f}(s_A + \bar{C}s_B)) / (B + t_{P,f}s_B)$$

where  $s_A$  and  $s_B$  are the standard errors of the constant term and slope of the calibration curve, and  $\bar{C}$  - the average concentration.

The numbers presented in Table were obtained under the following conditions: probability  $P = 99\%$ , number of points  $n = 10$ , number of degrees of freedom  $f = n - 2$ , and  $\bar{C} = 0.5 \text{ mg/dm}^3$  for resorcinol series phenols and  $\bar{C} = 50 \text{ mg/dm}^3$  for hydroxybenzene series phenols.

### Selectivity of the Method

As established experimentally, this method is selective for resorcinol series phenols and very sensitive. Steam distillable hydroxybenzene series phenols and non-phenolic admixtures present in waste waters form colourless cobalt-nitroso-complex, or those complexes, if formed, have colour intensity essentially less than that of resorcinol alkyl derivatives. As the equilibrium of complex formation to some extent depends on ionic strength, the calibration curves for solutions of high salt concentration have to be made using the method of admixtures.

### Conclusions

1. A new selective colorimetric method for the determination of resorcinol series phenols as cobalt-nitrosoalkylresorcinolates in solutions containing hydroxybenzene series phenols has been developed.
2. According to the method, the sample containing 0.001-0.025 mg resorcinol series phenol, 1 cm<sup>3</sup> 2.5·10<sup>-2</sup> M cobalt sulphate solution in acetate buffer (161 g/dm<sup>3</sup> CH<sub>3</sub>COONa·H<sub>2</sub>O and 7.56 g/dm<sup>3</sup> CH<sub>3</sub>COOH), and 2 ml 2.5 M NaNO<sub>2</sub> is transferred into a 25 cm<sup>3</sup> volumetric flask and made up with distilled water. The absorbance is measured after one hour in 5 cm cell against the zero absorbance of the reagent blank at 420 nm.
3. The slope of calibration curves depends on the compound under study; 5 cm light path gives following values: resorcinol - 0.975 (± 0.016); 5-methylresorcinol - 0.847 (± 0.003); 2,5-dimethylresorcinol - 0.432 (± 0.005) dm<sup>3</sup>/mg. The minimum concentration which can be measured ( $P = 99\%$ ) is 0.01-0.06 mg/dm<sup>3</sup>.

The applicability of this method for testing the total amount of resorcinol series phenols in waste water is described in [10].

## Acknowledgements

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