

<https://doi.org/10.3176/oil.2001.4.06>

# OIL SHALE RESORCINOLS – EFFECTIVE REAGENTS FOR NITRITE. AN ALGORITHM FOR THE INFLUENCE OF pH ON OPTICAL DENSITY

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*The theoretical basis is presented for testing nitrite with alkylresorcinols, the main water-soluble phenolic compounds of oil shale origin. An algorithm is deduced to describe the joint effect of pH and concentration of the reagents on the optical density (E). Acidic dissociation of the nitrosation products of 5-methylresorcinol and of the cobalt and iron (II) nitroso-5-methyl resorcinolate complexes is studied. Formation of a colloidal suspension is considered. The effect of pH on the contributions to E of the five coloured species formed is described. Acidic dissociation constants, molar extinction coefficients, stability constants, and solubility products of the species formed are estimated.*

## Introduction

Recently a new test method was presented [1] for photometric estimation of nitrite with alkylresorcinols, the main water-soluble phenolic compounds of oil shale origin. An algorithm was deduced [2] to describe the concentration effect of the reagents applied for formation of the coloured nitrosoalkylresorcinolate complex ( $\text{MeA}_n$ ). In the paper [2] the stability of  $\text{MeA}_n$  was expressed by means of the optical density measured ( $E$ ) and the initial concentrations of nitrite ( $C_N$ ) and the cation applied ( $C_{\text{Me}}$ ) as follows:

$$\beta_H = (E/\epsilon_H) / \{ C_{\text{Me}}(C_N - nE/\epsilon_H)^n \} \quad (1)$$

where  $\beta_H$  was the apparent stability constant, and  $\epsilon_H$  was the apparent molar extinction coefficient, both valid at the optimum pH only ( $\text{pH}_{\text{Co}} = 4.0$ ,  $\text{pH}_{\text{Fe}} = 3.3$ ). The value of  $n$  was 3 for cobalt complexes and 2 for iron com-

plexes. The unknown values of  $\beta_H$  and  $\epsilon_H$  were found from the coefficients of the linear relationship between  $(E/C_{Me})^{1/n}$  and  $E$  when the main oil shale originated phenols, 5-methylresorcinol (5-MR) or 2,5-dimethylresorcinol (2,5-DMR), and cobalt or iron(II) sulphate were applied as reagents. A twice higher sensitivity was found for the cobalt complexes formed with 5-MR compared with 2,5-DMR.

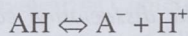
In this work, the essence of the joint effect of pH and concentrations of the reagents on the optical density was studied. To solve the problem, an algorithm for the prediction of  $E$  was deduced where the acidic dissociation of both nitrosoalkylresorcinol and the complex, as well as the complex stability and solubility were considered. The effect of pH on the partial contributions to the  $E$  values of the five coloured species formed were described. The characteristic constants of the participating equilibrium reactions were estimated using the most promising reagents established in [1], 5-MR as alkylresorcinol, and iron(II) and cobalt cations as Me.

## Theoretical Approach

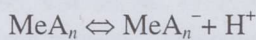
### Relationship between $E$ , $C_N$ , $C_{Me}$ and pH in Solutions of $MeA_n$

Equation (1) assumes that the equilibrium concentration of the complex formed depends on the total concentration of nitrosoalkylresorcinol remained after the complex formation.

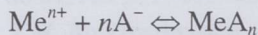
Actually, both nitrosoalkylresorcinol and the complex, as weak acids, can occur in two forms of coloured species:



and



According to the complex formation reaction



the complex is in equilibrium with the anionic species ( $A^-$ ) only. To describe the effect of pH on  $E$ , Equation (1) should be modified taking into account the dissociation percentages and contributions of the coloured species formed. The dissociation coefficients  $K_1$  and  $K_2$  are expressed as follows

$$K_1 = x_2[H^+]/x_1 \quad (2)$$

$$K_2 = x_4[H^+]/x_3 \quad (3)$$

where  $x_1$ ,  $x_2$ ,  $x_3$  and  $x_4$  represent the equilibrium concentrations of AH,  $A^-$ ,  $MeA_n$  and  $MeA_n^-$ , respectively.

According to the nitrite test-method proposed in [1],  $C_{Me}$  should be some orders higher than  $C_N$ . Then the approximation

$$[Me] = C_{Me} \quad (4)$$

can be applied.

When, thanks to the prescribed excess of alkylresorcinol, practically all nitrite is applied for nitrosation, the mass balance of nitrite, the stability constant of the complex ( $\beta$ ) and the optical density measured are compiled as follows:

$$C_N = x_1 + x_2 + nx_3 + nx_4 \quad (5)$$

$$\beta = (x_3 + x_4)/(C_{Me}x_2^n) \quad (6)$$

$$E = \varepsilon_1x_1 + \varepsilon_2x_2 + \varepsilon_3x_3 + \varepsilon_4x_4 \quad (7)$$

where  $\varepsilon$  with indexes 1–4 represent the molar extinction coefficients of the corresponding species.

#### Algorithm for Estimation of $\beta$ and $\varepsilon_3$

Equation (6) gives for the total concentration of the complex the expression

$$x_3 + x_4 = \beta C_{Me}x_2^n \quad (8)$$

According to Equations (2)–(5), the concentrations of the other coloured species formed can be related with the total concentration of the complex as follows

$$x_4 = K_2(x_3 + x_4)/(K_2 + [H^+]) \quad (9)$$

$$x_3 = x_4[H^+]/K_2 \quad (10)$$

$$x_2 = K_1[C_N - n(x_3 + x_4)]/(K_1 + [H^+]) \quad (11)$$

$$x_1 = [H^+][C_N - n(x_3 + x_4)]/(K_1 + [H^+]) \quad (12)$$

Substitution of Equations (9)–(12) into Equation (7) and replacements give for the total concentration of the complex the pH-dependence

$$x_3 + x_4 = (K_2 + [H^+])[E(K_1 + [H^+]) - C_M(\varepsilon_1[H^+] + \varepsilon_2K_1)]/[\varepsilon_3(K_1 + [H^+])(qK_2 + [H^+]) - n(\varepsilon_1[H^+] + \varepsilon_2K_1)(K_2 + [H^+])] \quad (13)$$

where the ratio of the molar extinction coefficients

$$q = \varepsilon_4/\varepsilon_3 \quad (14)$$

was applied because the direct estimation of  $\varepsilon_4$  and  $\varepsilon_3$  was unrealisable. This problem will be discussed in more detail farther below.

Substitution of Expressions (13) and (11) for  $(x_3 + x_4)$  and  $x_2$  in Equation (6) and replacements result the algorithm for the stability constant

$$\beta = (K_2 + [\text{H}^+])[E(K_1 + [\text{H}^+]) - C_N(\varepsilon_1[\text{H}^+] + \varepsilon_2 K_1)] / [\varepsilon_3(K_1 + [\text{H}^+])(qK_2 + [\text{H}^+]) - n(\varepsilon_1[\text{H}^+] + \varepsilon_2 K_1)(K_2 + [\text{H}^+])] / \{K_1[C_N - n(x_3 + x_4)] / (K_1 + [\text{H}^+])\}^n / C_{\text{Me}} \quad (15)$$

The unknown values of the constants  $\beta$  and  $\varepsilon_3$  can be computed from Equation (15) by the least squares method. The values of  $K_1$ ,  $K_2$ ,  $\varepsilon_1$ ,  $\varepsilon_2$ , and  $q$  should be known before. Estimation of these constants by special series of experiments will be described later.

### Algorithm for Prediction of $E$

When all the constants have been found, the optical density of the solution at any pH can be predicted using the algorithm

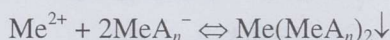
$$E = \varepsilon_1[\text{H}^+][C_N - n(x_3 + x_4)] / (K_1 + [\text{H}^+]) + \varepsilon_2 K_1 [C_N - n(x_3 + x_4)] / [(K_1 + [\text{H}^+]) + \varepsilon_3(x_3 + x_4)[\text{H}^+] / (K_2 + [\text{H}^+]) + q\varepsilon_3 K_2(x_3 + x_4) / (K_2 + [\text{H}^+])] \quad (16)$$

where  $(x_3 + x_4)$  should be calculated from Equation (13).

It is noteworthy that a turbidity can arise in the solutions of the complexes near the optimum pH. In such cases Equation (16) is not valid. Next, an approach for modelling of the turbid solutions will be discussed.

### Relationship between $E$ , $C_N$ , $C_{\text{Me}}$ and pH in Turbid Solutions

The arising turbidity can be explained by the reaction between cations and anionic species of the complex whose amount increases with increasing pH:



The solubility product of the precipitate ( $P$ ) is expressed by the equation

$$P = C_{\text{Co}} x_4^2 \quad (17)$$

Consequently, concentration of the anionic species of the complex should be constant in turbid solutions and is fixed by the cation concentration as follows:

$$x_4 = (P/C_{\text{Co}})^{1/2} \quad (18)$$

Concentrations of the other coloured species depend on pH and are determined by the characteristic coefficients and by the unchangeable under the test conditions values of  $x_4$  and  $C_{\text{Me}}$  as follows:

$$x_3 = x_4[\text{H}^+] / K_2 \quad (19)$$

$$x_3 + x_4 = x_4(K_2 + [\text{H}^+]) / K_2 \quad (20)$$

$$x_2 = [x_4(K_2 + [\text{H}^+]) / (K_2 C_{\text{Me}} \beta)]^{1/m} \quad (21)$$

$$x_1 = [x_4(K_2 + [\text{H}^+]) / (K_2 C_{\text{Me}} \beta)]^{1/m} [\text{H}^+] / K_1 \quad (22)$$

When, thanks to a sufficient excess of alkylresorcinol, practically all nitrite is applied for nitrosation, the mass balance of nitrite is expressed as

$$C_N = x_1 + x_2 + nx_3 + nx_4 + 2nx_5 \quad (23)$$

where  $x_5$  is the molar concentration of the indissoluble species in the bulk of solution.

Equation (23) gives for the concentration of the indissoluble species the expression

$$x_5 = (C_N - x_1 - x_2 - nx_3 - nx_4)/2n \quad (24)$$

Alike Equation (7), the optical density of turbid solutions is compiled from the partial extinctions of the coloured species

$$E = \varepsilon_1 x_1 + \varepsilon_2 x_2 + \varepsilon_3 x_3 + \varepsilon_4 x_4 + \varepsilon_5 x_5 \quad (25)$$

### Algorithm for Estimation of $P$ and $\varepsilon_5$

Equations (24) and (25) give for the molar extinction coefficient of the colloidal particles the expression

$$\varepsilon_5 = 2n(E - \varepsilon_1 x_1 - \varepsilon_2 x_2 - \varepsilon_3 x_3 - \varepsilon_4 x_4)/(C_N - x_1 - x_2 - nx_3 - nx_4) \quad (26)$$

Substitution of the concentrations in Equation (26) with their expressions in Equations (18), (19), (21), and (22) and (24) gives a relationship which includes two unknown constants,  $P$  and  $\varepsilon_5$ . The values of the constants can be computed by the least squares method.

### Algorithm for Prediction of $E$ in Turbid Solutions

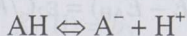
When all the constants have been found, the optical density at any pH in the region of colloidal solutions can be calculated by the algorithm

$$\begin{aligned} E = & \varepsilon_1 [H^+] [(P/C_{Co})^{1/2} (K_2 + [H^+]) / (K_2 C_{Me} \beta)]^{1/n} / K_1 + \\ & + \varepsilon_2 \{ (P/C_{Co})^{1/2} (K_2 + [H^+]) / (K_2 C_{Me} \beta) \}^{1/n} + \varepsilon_3 (P/C_{Co})^{1/2} [H^+] / K_2 + \varepsilon_4 (P/C_{Co})^{1/2} + \\ & + \varepsilon_5 \{ (C_N - [H^+] [(P/C_{Co})^{1/2} (K_2 + [H^+]) / (K_2 C_{Me} \beta)]^{1/n} / K_1 - [(P/C_{Co})^{1/2} (K_2 + \\ & + [H^+]) / (K_2 C_{Me} \beta)]^{1/n} - n(P/C_{Co})^{1/2} [H^+] / K_2 - n(P/C_{Co})^{1/2} \} / 2n \end{aligned} \quad (27)$$

### Algorithms for Estimation of $K_1$ , $K_2$ , $\varepsilon_1$ , $\varepsilon_2$ , and $\varepsilon_4/\varepsilon_3$

Dissociation characteristics of any coloured reagent can be easily found from a series of extinction values estimated at various pH values.

For any acidic dissociation



the dissociation coefficient, the mass balance of the species, and the optical density measured are described by the formulas

$$K = [A^-][H^+]/[AH] \quad (28)$$

$$C = [AH] + [A^-] \quad (29)$$

$$E = \varepsilon_1[AH] + \varepsilon_2[A^-] \quad (30)$$

### Approach I

When an acidic dissociation is practically completed at higher values of pH, a steady state of the optical density ( $E_A$ ) should be obtained. Then the value for  $\varepsilon_2$  can be found easily from

$$\varepsilon_2 = E_A/C \quad (31)$$

Combining Equations (28)–(31) gives the auxiliary relationship

$$(E_A - E)/[H^+] = -\varepsilon_1 C/K + E/K \quad (32)$$

which represents a linear regression

$$Y_1 = a_1 + b_1 E \quad (33)$$

of the function

$$Y_1 = (E_A - E)/[H^+] \quad (34)$$

versus optical density measured.

The formulas of the regression coefficients

$$a_1 = -\varepsilon_1 C/K \quad (35)$$

$$b_1 = 1/K \quad (36)$$

allow to calculate the acidic dissociation characteristics from the slope and intercept of the straight line (33) as follows

$$K = 1/b_1 \quad (37)$$

$$\varepsilon_1 = -a_1/(b_1 C) \quad (38)$$

### Approach II

When a constant value of the optical density for the molecular form ( $E_{AH}$ ) is evident at the lower region of pH values, it is easy to calculate the extinction coefficient for AH by

$$\varepsilon_1 = E_{AH}/C \quad (39)$$

Combining Equations (28)–(30) and (39) gives the auxiliary relationship

$$[H^+](E - E_{AH}) = \varepsilon_2 C/K - E/K \quad (40)$$

which represents a linear regression

$$Y_2 = a_2 - b_2E \quad (41)$$

where the function value is calculated by means of the experimental data as follows

$$Y_2 = [H^+](E - E_{AH}) \quad (42)$$

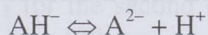
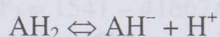
The dissociation characteristics can be found from the plot of  $Y_2$  versus  $E$  by analogy to the plot of  $Y_1$  versus  $E$  as

$$K = 1/b_2 \quad (43)$$

$$\varepsilon_2 = a_2/(b_2C) \quad (44)$$

### Algorithm for Estimation of $K_1(\text{II})$ and $\varepsilon_2(\text{II})$ for Dissociation of Two-Basic Acids

Dissociation of a two-basic acid,  $\text{AH}_2$ , involves two consecutive reactions



with dissociation coefficients  $K_1(\text{I})$  and  $K_1(\text{II})$ , and molar extinction coefficients  $\varepsilon_1$ ,  $\varepsilon_2(\text{I})$  and  $\varepsilon_2(\text{II})$ .

The characteristics of the first dissociation,  $K(\text{I})$ ,  $\varepsilon_1$  and  $\varepsilon_2(\text{I})$ , can be found following *Approach II* under the acidic conditions where the second dissociation is negligible.

Characteristics of the second dissociation can be found as follows.

Co-solution of the relationships

$$K_1(\text{I}) = [\text{AH}^-][\text{H}^+]/[\text{AH}_2] \quad (45)$$

$$K_2(\text{II}) = [\text{A}^{2-}][\text{H}^+]/[\text{AH}^-] \quad (46)$$

$$C = [\text{AH}_2] + [\text{AH}^-] + [\text{A}^{2-}] \quad (47)$$

$$E = \varepsilon_1[\text{AH}_2] + \varepsilon_2(\text{I})[\text{AH}^-] + \varepsilon_2(\text{II})[\text{A}^{2-}] \quad (48)$$

enables to compile a linear regression

$$Y_3 = a_3 - b_3E \quad (49)$$

where

$$Y_3 = [H^+]^2(E - C\varepsilon_1)/K_1(\text{I}) + [H^+](E - C\varepsilon_2(\text{I})) \quad (50)$$

$$a_3 = \varepsilon_2(\text{II})CK_1(\text{II}) \quad (51)$$

$$b_3 = K_1(\text{II}) \quad (52)$$

The characteristics can be found from the coefficients of Regression (49) by analogy to *Approach I* and *Approach II* as follows:

$$K_1(\text{II}) = b_3 \quad (53)$$

$$\varepsilon_2(\text{II}) = a_3/(b_3C) \quad (54)$$

### Algorithm for Estimation of $K_2$ and $q$ for the Complexes

The complex  $\text{MeA}_n$  obtains characteristics of a moderately weak acid because the electron density distribution in the complex promotes the acidic dissociation of the second OH-group of nitroso-5-MR. To estimate the values for  $\epsilon_3$  and  $\epsilon_4$  the authentic concentration of the complex in the solution should be known. Unfortunately, concentration of the solution obtained by equilibrium processes of formation, solid-phase extraction and re-extraction is uncertain. So, instead of the absolute value, the ratio  $q = \epsilon_4/\epsilon_3$  should be found as the equivalent to the ratio  $E_A/E_{\text{AH}}$ . When the optical density for the anionic form  $E_A$  is known, that for the molecular form  $E_{\text{AH}}$  as well  $K_2$  can be estimated from the coefficients of the linear relationship (32) where  $\epsilon_1 C$  is replaced by  $E_{\text{AH}}$

$$(E_A - E)/[\text{H}^+] = -E_{\text{AH}}/K_2 + E/K_2 \quad (55)$$

### Experimental, Computation and Discussion

#### Estimation of $K_1$ , $\epsilon_1$ , and $\epsilon_2$ for 4-Nitroso-5-Methylresorcinol and 2,4-Dinitroso-5-Methylresorcinol

The reaction products of nitrous acid with 5-MR, 4-nitroso-5-methylresorcinol (AH) and 2,4-dinitroso-5-methylresorcinol ( $\text{AH}_2$ ) are new commercially not obtainable reagents. Therefore, for this work, the reagents were synthesised according to the procedures described in [3].

For estimation of the dissociation characteristics of the nitroso compounds their  $2 \times 10^{-4} \text{ M}$  solutions in 0.01M  $\text{H}_2\text{SO}_4$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{COONa}$ , or  $\text{NaOH}$  were mixed to obtain series with pH 2–12.

The plots of  $E$  (recorded on the SPEKOL 11 at 420 nm in cells 10 mm) versus pH (measured using METLER-TOLEDO 320 pH meter) are depicted in Fig. 1a.

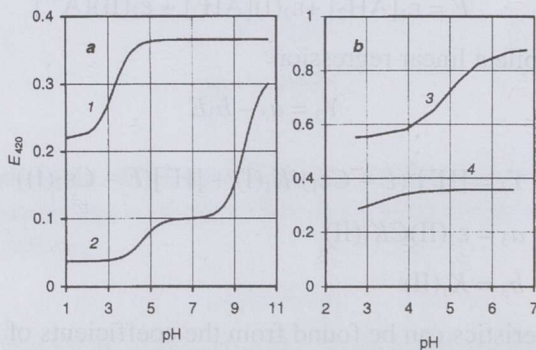


Fig. 1. Plot of optical density versus pH for: a –  $2 \times 10^{-4} \text{ M}$  solutions of 4-nitroso-5-methylresorcinol (curve 1) and 2,4-dinitroso-5-methylresorcinol (curve 2); b – eluted concentrate of  $\text{CoA}_3$  (curve 1) and  $\text{FeA}_2$  (curve 2)



The results give a one-step curve (1) for the mono-nitroso compound with dissociation coefficient  $K_1$ . The practically unchanging optical density,  $E_A = 0.365$ , is evident for this curve above pH 5–5.5. So, *Approach I* can be applied. The experimental data depicted in Fig. 1a yield for mono-nitroso-5-methylresorcinol the auxiliary function

$$Y_1 = 398 - 1825E \quad (56)$$

A significantly lower two-step curve (2) is evident for the dinitroso-5-methylresorcinol. The steady state of  $E$  for the anionic species of the dinitroso compound,  $A^{2-}$ , cannot be obtained in the pH region studied. So, in this case, *Approach II* is more appropriate. A practically constant optical density can be fixed for  $AH_2$  between pH 2–2.5. Using this value,  $E_{AH} = 0.037$ , the auxiliary function (40) for the first dissociation of  $AH_2$  obtains the trend line

$$Y_2 = 1541 - 41667E \quad (57)$$

The auxiliary function  $Y_3$  for the second dissociation (50) depends, according to Equation (49), on  $E$  as follows:

$$Y_3 = 1580 - 3.03 \times 10^9 E \quad (58)$$

The dissociation characteristics of the nitroso compounds calculated from Equations (37), (38), (43), (44), (53) and (54) by means of the coefficients in Equations (56)–(58) are presented in Table 1.

**Table 1. Dissociation and Molar Extinction Coefficients of 4-Nitroso-5-Methylresorcinol (AH) and 2,4-Dinitroso-5-Methylresorcinol ( $AH_2$ )**

	$K_1$ or $K_1(I)$	$K_1(II)$	$\epsilon_1$	$\epsilon_2$ or $\epsilon_2(I)$	$\epsilon_2(II)$
AH	$5.48E - 04$	–	1096	1827	–
$AH_2$	$2.40E - 05$	$3.30E - 10$	185	500	1,580

### Estimation of $K_2$ and $\epsilon_4/\epsilon_3$ for the Complexes

The reagent grade complexes are required to estimate the dissociation characteristics. For this aim  $CoA_3$  and  $FeA_2$  were separated from the excess of the reagents by solid phase disk-extraction on the J. T. Baker *Speedisk* SDB, washed with water and eluted with ethanol. The aliquots of the concentrates obtained were diluted to 1 : 1 with various pH buffer solutions. Thereafter, immediately their optical density was estimated. A notable effect of pH on the optical density of the complexes in Fig. 2 proves that the acidic dissociation of the complexes takes place. The auxiliary curves calculated according to Equation (32) starting from  $E_A = 0.88$  for  $CoA_3$  and  $E_A = 0.368$  for  $FeA_2$  obtain the trend lines

$$Y_{1_{\text{Co}}} = -50097 + 9091E \quad (59)$$

$$Y_{1_{\text{Fe}}} = -1852 + 501E \quad (60)$$

The dissociation characteristics of the complexes calculated from the coefficients of Regressions (59) and (60) are given in Table 2.

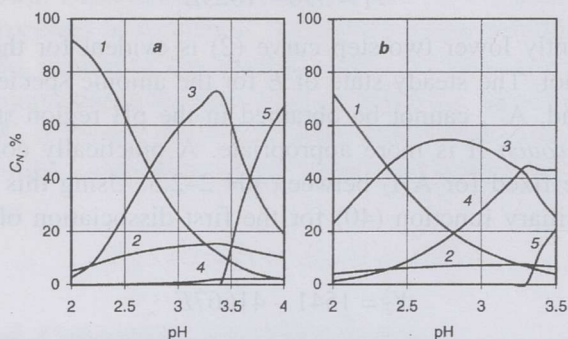


Fig. 2. Effect of pH on the distribution of species at formation of: *a* –  $\text{CoA}_3$ ; *b* – of  $\text{FeA}_2$ . Curves: 1 – AH; 2 –  $\text{A}^-$ ; 3 –  $\text{MeA}_n$ ; 4 –  $\text{MeA}_n^-$ ; 5 –  $\text{Me}(\text{MeA}_n)_2$

Table 2. Characteristics of the Complexes

	$K_2$	$q$	$\epsilon_3$	$\epsilon_4$	$\epsilon_5$	$\beta$	$P$
$\text{CoA}_3$	$1.10E-05$	1.597	22,000	35,134	53,300	$1.37E+13$	$2.43E-16$
$\text{FeA}_2$	$5.40E-04$	1.361	9,080	12,360	51,400	$7.83E+08$	$2.43E-13$

## Discussion about the Reaction Products

The mathematical models deduced in the theoretical part of this paper were applied and proved using the experimental data from our previous paper [1]. The first two columns in Table 3 represent the experimental data. At that, the values of optical density measured are reduced to the cell length 1 cm ( $E = E_{\text{exp}}/l$ ).

When pH is 2, the complex formation is negligible. So, the values of the optical density found must represent mainly absorbance of the molecular species of the nitroso compound AH or  $\text{AH}_2$  formed. According to Table 1, when  $C_N$  is  $5 \times 10^{-5} \text{M}$ , the  $E$  value for the mononitroso compound should be 0.055, and for the dinitroso compound only 0.005. The estimated optical density of the cobalt solution is 0.072 and iron(II) solution 0.099. Therefore, the formation of the mononitroso compound, AH, can be observed in very diluted nitrite solutions with the concentration of 5-MR several orders higher. As previously established [2], cobalt cations form the complex  $\text{CoA}_3$  with AH, and the iron(II) cations –  $\text{FeA}_2$ . According to the precipitation reaction, the corresponding indissoluble salts should be  $\text{Co}(\text{CoA}_3)_2$  and  $\text{Fe}(\text{FeA}_2)_2$ .

Table 3. Estimation of  $\beta$  and  $\varepsilon_3$  ( $C_N = 5E-5M$ ,  $C_{AR} = 0.01M$ ,  $C_{Me} = 0.002M$ )

pH	$E$	$[H^+]$	$(x_3 + x_4)$ (Eq. (13))	$x_2$ (Eq. (11))	$\beta$ (Eq. (15))	$(\beta_{\text{mean}} - \beta)^2$	$E_{\text{calc}}$ (Eq. (16))
CoA <sub>3</sub> , for $\varepsilon_3 = 22,000$							
2	0.072	0.01	8.22E-07	2.47E-06	2.73E+13	1.84E+26	0.065
2.2	0.087	0.00631	1.58E-06	3.62E-06	1.67E+13	8.57E+24	0.083
2.4	0.112	0.003981	2.86E-06	5.01E-06	1.13E+13	5.78E+24	0.121
2.6	0.171	0.002512	5.97E-06	5.75E-06	1.57E+13	3.87E+24	0.165
2.8	0.203	0.001585	7.61E-06	6.98E-06	1.12E+13	6.50E+24	0.211
3	0.245	0.001	9.81E-06	7.29E-06	1.27E+13	1.14E+24	0.248
3.2	0.272	0.000631	1.12E-05	7.66E-06	1.24E+13	1.70E+24	0.275
3.4	0.298	0.000398	1.25E-05	7.28E-06	1.62E+13	5.92E+24	0.295
3.6	0.322	0.000251	1.36E-05	6.24E-06	2.81E+13	2.06E+26	0.309
3.8	0.37	0.000158	1.61E-05	1.42E-06	2.83E+15	7.90E+30	0.321
4	0.384	0.0001	1.64E-05	6.09E-07	3.64E+16	1.32E+33	0.331
4.2	0.4	6.31E-05	1.67E-05	-1.20E-07	-4.80E+18	2.30E+37	0.344
$\Sigma$ :					9.62E+13	3.35E+25	
Mean:					1.37E+13	4.78E+24	
$s_\beta$ , %:					15.9		
FeA <sub>2</sub> , for $\varepsilon_3 = 9,080$							
2	0.099	0.01	6.06E-06	1.97E-06	7.82E+08	5.20E+11	0.099
2.2	0.126	0.00631	9.71E-06	2.44E-06	8.14E+08	9.27E+14	0.125
2.4	0.153	0.003981	1.32E-05	2.85E-06	8.10E+08	7.25E+14	0.152
2.6	0.175	0.002512	1.58E-05	3.31E-06	7.22E+08	3.76E+15	0.177
2.8	0.199	0.001585	1.84E-05	3.42E-06	7.87E+08	1.17E+13	0.198
3	0.217	0.001	1.98E-05	3.65E-06	7.46E+08	1.37E+15	0.218
3.2	0.235	0.000631	2.11E-05	3.59E-06	8.21E+08	1.46E+15	0.235
3.3	0.244	0.000501	2.17E-05	3.40E-06	9.38E+08	2.39E+16	0.242
3.4	0.298	0.000398	2.80E-05	-3.48E-06	1.16E+09	1.38E+17	0.249
3.5	0.334	0.000316	3.19E-05	-8.74E-06	2.09E+08	3.30E+17	0.254
$\Sigma$ :					5.48E+09	8.26E+15	
Mean:					7.83E+08	1.18E+15	
$s_\beta$ , %:					4.39		

### Estimation of $\beta$ and $\varepsilon_3$

The experimental data of  $E$  and pH from Table 3 and the dissociation characteristics for AH and CoA<sub>3</sub> from Tables 1 and 2 were applied to compute  $\beta$  and  $\varepsilon_3$  for CoA<sub>3</sub> by Algorithm (15) in Microsoft Excel. For this aim, various values of  $\varepsilon_3$  were fed until the least squares dispersion of  $\beta$  from its mean was obtained at various pH values. At that, for every  $\varepsilon_3$  the values of  $(x_3 + x_4)$  were calculated using Equation (13). The computation gives the most suitable molar extinction coefficient,  $\varepsilon_3 = 22,000$  in the pH region 2–3.4, resulting in the value  $1.37(\pm 0.22) \times 10^{13}$  for  $\beta$ . A systematic illogical de-

crease in  $x_2$  and increase in  $\beta$  with increasing pH is revealed above pH 3.4 inasmuch as the solutions turned turbid. The turbid region is shadowed in the tables and is excluded in the calculations of dispersion percentages,  $s_\beta$ .

Estimation of  $\beta$  and  $\epsilon_3$  for  $\text{FeA}_2$  was carried out following the same procedure as for  $\text{CoA}_3$ . The computation gives for  $\epsilon_3$  of  $\text{FeA}_2$  in the region pH 2–3.2 the best value 9,080, which results in the value  $7.83(\pm 1.33) \times 10^8$  for  $\beta$ . Analogous to the cobalt complex, homogeneous turbidity was evident before the precipitate fell out in the solutions. Likewise, the inconsistent decrease in  $x_2$  and increase in  $\beta$  were obtained using Equations (13) and (15) for the turbid solutions between pH 3.4–3.5. Contributions of the dissoluble colloidal species will be discussed below.

The theoretical data for  $E$  in real solutions computed by Algorithm (16) using the constants and coefficients found are presented in the last column of Table 3. The theoretical results agree satisfactory with the corresponding experimental data in the second column.

When pH exceeded 3.5 for  $\text{Fe}(\text{FeA}_2)_2$  and 4.2 for  $\text{Co}(\text{CoA}_3)_2$ , the photometric method was unsuitable since a flake precipitate formed.

### Estimation of $P$ and $\epsilon_5$

The turbid solutions were modelled by Algorithm (26). Table 4 presents the course of the calculations where the solvation product,  $P$ , was computed as the value enabling the least dispersion percentage of  $\epsilon_5$  from its mean under the pH region examined. At first, the unchangeable  $x_4$  was calculated from Equation (18) for the  $P$  values suggested. Thereafter,  $x_3$ ,  $(x_3 + x_4)$ ,  $x_2$ ,  $x_1$  and  $x_5$  were calculated using the Equations (18)–(22) and (24). Knowing the concentrations of the five types of species and molar extinction coefficients of the soluble species, the value for  $\epsilon_5$  was computed from Equation (26). The computation gave the least dispersion of  $\epsilon_5$  for the colloidal cobalt compound,  $\epsilon_5 = 53,300(\pm 1679)$ , when  $P$  was  $2.43 \times 10^{-16}$ . It was found that the most fitting molar extinction coefficient for the colloidal iron(II) compound,  $\epsilon_5 = 514,000(\pm 44)$  could be obtained when  $P$  was  $2.34 \times 10^{-13}$ .

The theoretical data for  $E$  in turbid solutions computed by the algorithm (27) using the constants and coefficients found are presented in the last column of Table 4. The theoretical results agree satisfactory with the corresponding experimental data in the second column.

Table 4. Estimation of  $\varepsilon_5$  and  $P$  for Turbid Solutions ( $C_N = 5E-5M$ ,  $C_{AR} = 0.01M$ ,  $C_{Me} = 0.002M$ )

pH	$E$	$x_3$	$(x_3 + x_4)$	$x_2$	$x_1$	$x_5$	$\varepsilon_5$	$(\varepsilon_{mean} - \varepsilon_5)^2$	$E_{calc}$
<b>CoA<sub>3</sub>; <math>P = 2.43E - 16</math>, <math>x_4 = 3.49E - 07</math></b>									
3.4	0.298	1.26E - 5	1.30E - 05	7.79E - 6	5.66E - 06	-3.89E - 07	3.14E + 04	4.78E + 08	0.289
3.6	0.342	7.96E - 6	8.31E - 06	6.71E - 6	3.08E - 06	2.55E - 06	5.46E + 04	1,676,044	0.339
3.8	0.37	5.02E - 6	5.37E - 06	5.80E - 06	1.68E - 06	4.40E - 06	5.34E + 04	8,464,398	0.370
4	0.384	3.17E - 6	3.52E - 06	5.04E - 6	9.20E - 07	5.58E - 06	5.23E + 04	960,675.2	0.389
4.2	0.4	2.00E - 6	2.35E - 06	4.40E - 6	5.07E - 07	6.34E - 06	5.29E + 04	165,228.5	0.403
						$\Sigma$ :	2.13E + 05	2,810,413	
						Mean:	5.33E + 04		
						$S_p$ , %:	3.15		
<b>FeA<sub>2</sub>; <math>P = 2.34E - 13</math>, <math>x_4 = 1.08E - 05</math></b>									
3.3	0.244	1.00E - 05	2.09E - 05	3.65E - 06	3.34E - 06	3.25E - 07	2.72E + 04	5.88E + 08	0.252
3.4	0.298	7.96E - 06	1.88E - 05	3.46E - 06	2.52E - 06	1.61E - 06	5.15E + 04	965	0.298
3.5	0.334	6.32E - 06	1.72E - 05	3.31E - 06	1.91E - 06	2.62E - 06	5.14E + 04	965	0.334
						$\Sigma$ :	1.03E + 05	1931	
						Mean:	5.14E + 04		
						$S_p$ , %:	0.085		

## Distribution of the Species

Equations (8)–(12) and (18)–(22) were applied for evaluation of the pH effect on the distribution of various species. Figure 2 illustrates the distribution when the initial concentration of nitrite is  $5 \times 10^{-5} \text{M}$ , of 5-MR 0.01M and of the metal cation 0.002M. The curves in Fig. 2a demonstrate domination of the corresponding to pH molecular species, AH,  $\text{CoA}_3$  or  $\text{Co}(\text{CoA}_3)_2$ , (curves 1, 3 and 5). At that, the concentrations of the anionic forms,  $\text{A}^-$  and  $\text{CoA}_3^-$  (curves 2 and 4), are depressed by the reactions of complex formation and precipitation. A similar distribution of the species is evident in Fig. 2b for the iron (II) compounds. Only, thanks to the smaller  $P$  value, the share of the anionic species of the iron complex (curve 4) is higher and that of the indissoluble particles (curve 5) is lower.

Figure 3 demonstrates that the partial contribution of AH and  $\text{A}^-$  to the total optical density is negligible above pH 3. Under the optimum test conditions established in [1] for the cobalt compounds (pH 4) the colloidal particles  $\text{Co}(\text{CoA}_3)_2$  give the main contribution to  $E$  (Fig. 3a). Under the optimum conditions established for the iron compounds (pH 3.3) the anionic species  $\text{FeA}_2^-$  contribute most. When pH exceeds 3.3, the sensitivity of the method increases thanks to the addition of the contribution of  $\text{Fe}(\text{FeA}_2)_2$ . The latter form is inadvisable since the iron colloidal species are not stable and can precipitate in time.

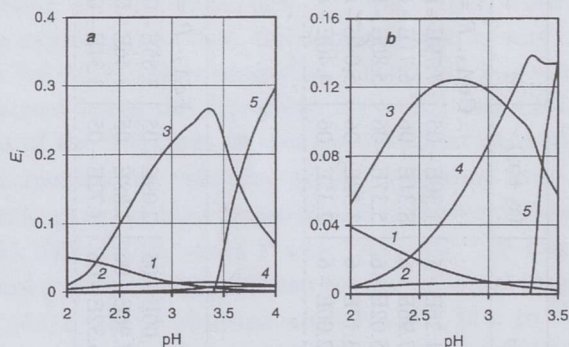


Fig. 3. Effect of pH on the partial contribution of the species from Fig. 2 on  $E$

## Conclusions

Alkylresorcinols, the main phenolic compounds obtained at oil shale retorting, can be applied as effective reagents for colorimetric determination of nitrite. An algorithm is deduced to explain the joint effect of the initial concentration of the reagents and pH on the optical density of the nitrite solution tested. The complicated relationship considers contributions of the five coloured species resulted from the acidic dissociations of nitrosoalkylresor-

cinol and the complex,  $AH$ ,  $A^-$ ,  $MeA_n$ ,  $MeA_n^-$ , and from the precipitation of an indissoluble salt,  $Me(MeA_n)_2$ . The theoretical optical densities computed using the acidic dissociation constants, complex stability constants, salt solubility product, and molar extinction coefficients found for 5-methylresorcinol and cobalt or iron(II) sulphate agree with the corresponding experimental results.

## Acknowledgements

The authors thank the Estonian Science Foundation for financial support for this study by Grant 3606.

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Presented by L. Mölder

Received June 12, 2001