OIL SHALE RESORCINOLS – EFFECTIVE REAGENTS FOR SPECTROPHOTOMETRIC DETERMINATION OF NITRITE

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A new test method for nitrite as nitrosoalkylresorcinolate is proposed. The method is based on the especially easy nitrosation of alkylresorcinols (R) with nitrous acid formed from nitrite in acidic solutions, and on the subsequent formation of a coloured complex with a transition metal cation (Me). The main oil shale originated phenols, 5-methylresorcinol and 2,5-dimethylresorcinol, are applied as R and the cobalt, nickel, copper and iron(II) cations as Me. Effect of nitrite, R, and Me concentration, and pH on the absorption is described. Under the optimum conditions found (0.01 mol dm^{-3} of 5-methylresorcinol and $CoSO_4$, pH 4), Beer's law is obeyed in the concentration region of nitrite 0.1–10 mg dm^{-3}.

Introduction

Nitrate and nitrite are widespread anions in the environment. They are found together in waters, soils and some food products. Both species are produced in the nitrification process when ammonia is oxidised by soil bacteria. Nitrate is leached in abundance from fertilizers and can be reduced to nitrite under anaerobic conditions. Nitrite is found in animal and plant tissues. Sodium and potassium nitrites and nitrates are used as food additives in cured meat.

The increased nitrate and nitrite content indicates the contamination of water. The potential health danger is concerned from immoderate nitrate and nitrite content in food products because of the possibility to form carcinogenic *N*-nitrosoamines. So, testing of nitrate and nitrite in water samples, soils and food products is important. Numerous analytical methods for nitrate involve reduction of nitrate to nitrite prior spectrophotometric determination of the nitrite formed.

The nitrite standard test methods [1–3] and their modifications [4, 5] are based on the reaction of nitrite with an aromatic amine (sulfanilamide, sulfapyridine, sulfathiazole) to form a diazonium salt, and the following reaction with a coupling reagent (1-naphtol-4-sulphonate, N-1-(naphtyl)-ethylenediamine) to produce a highly-coloured azo dye.

We have recently claimed a simple and less toxic test method for nitrite [6]. The new method is based on the formation of a coloured nitrosoalkylresorcinolate complex. Earlier, the analogical cobalt complex was applied by us [7] for determination of resorcinol and its alkyl derivatives according to the consequent reactions

$$nHNO_2 + R = (NO)_nR + nH_2O \qquad (1)$$

and

$$mR(NO)_n + Me^{2+} = Me[(NO)_nR]_m + (2-m)H^+ \qquad (2)$$
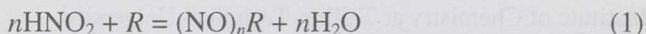
where Me^{2+} was cobalt cation.

It was found that the number of nitroso substituents n was 1, when R was dialkylresorcinol or 2-alkylresorcinol, and 2 when R was resorcinol, 5- or 4-alkylresorcinol. The number of ligands in the complex m was 3 for mono-nitroso compounds, and 2 for dinitroso compounds.

When an alkylresorcinol in diluted solutions (below 10^{-4} mol dm^{-3}) was used as the analyte, an excess of the reagents was required (0.1 mol dm^{-3} of $NaNO_2$ and 0.001 mol dm^{-3} of $CoSO_4$) to obtain the adequate nitrosation and the subsequent complex formation.

The aim of the present work was to found optimum conditions for the formation of $Me[(NO)_nR]_m$ using nitrite in diluted solutions (below $1 \times \times 10^{-3}$ mol dm^{-3}) as the analyte. Effect of the concentration of reagents, pH, reaction time and diverse salts on the optical density is described. In this work, the two main components of oil shale originated phenols, 5-methyl-resorcinol (5-MR) and 2,5-dimethylresorcinol (2,5-DMR), are examined as R. Besides cobalt cations, applied for determination of alkylresorcinols, the metal cations, Fe^{+2}, Ni^{+2} and Cu^{+2}, reported in the paper [8] to form coloured nitroso complexes, are tested for determination of nitrite.

Experimental

Reagents and Apparatus

All chemicals used were of analytical-reagent grade, except 5-MR (99 %) and 2,5-DMR (98.4 %) separated from oil shale phenols at the former RAS *Kiviter* and at the Institute of Chemistry.

Nitrite stock standard solution, 0.01 mol dm^{-3}, was prepared by dissolving 0.6901 g of sodium nitrite, dried for 24 h in a desiccator containing concentrated sulfuric acid, in 1000 cm^3 of distilled water.

Nitrite working standard solution was diluted from the appropriate volume of the stock solution on the day of sampling.

***R* solution**, 0.05 mol dm^{-3}, was prepared by dissolving 3.55 g of 5-MR × × H_2O or 3.455 g of 2,5-DMR in 500 cm^3 of distilled water. The solution was prepared freshly when it turned yellowish.

Me^{2+} solution, 0.05 mol dm^{-3}, was prepared by dissolving 3.88 g of dried at 450 °C $CoSO_4$, 3.87 g of dried at 300 °C $NiSO_4$ or 3.12 g of $CuSO_4$ × $5H_2O$ in 500 cm^3 of distilled water, or by dissolving 6.95 g of $FeSO_4$ × $7H_2O$ in 500 cm^3 of 0.05 mol dm^{-3} acetic acid preserved with 1 cm^3 chloroform.

pH buffers were prepared by mixing an appropriate ratio of 0.1 mol dm^{-3} solutions of CH_3COOH and alkali.

The optical density of the samples was recorded by a spectrophotometer SPECOL 10. The pH values were measured by a METLER TOLEDO pH-meter 320.

Procedure

In the series aimed to establish the optimum conditions for the determination of nitrite, an aliquot of the 2.5 × 10^{-4} mol dm^{-3} of *nitrite working standard solution* was transferred into a 25 cm^3 flask, and the *buffer solution, Me^{2+} solution* and *R solution* were added. The sample volume was adjusted to 25 cm^3 with distilled water. The absorbtion *E* of the yellow complex formed was measured after certain time intervals in cells 0.5–5 cm at 420 nm.

Results and Discussion

Effect of pH

According to the Reactions (1) and (2), the maximum formation of the coloured complex $Me[(NO)_nR]_m$ would be obtained when all the nitrite species were protonated to the molecular form HNO_2, and all the nitrosed alkyl-resorcinol species, on the contrary, were dissociated to the anionic form. The actual optimum pH depends on acidic dissociation, concentration of the reagents, stability of the nitrosoalkylresorcinolate complex formed, and the kinetics of the Reactions (1) and (2).

Figure 1 illustrates the plot of optical density *E* for 5 × 10^{-5} mol dm^{-3} of nitrite (0.7 mg dm^{-3} N-NO_2^-) versus pH when concentration of 5-MR or 2,5-DMR is 0.01 mol dm^{-3} and concentration of the cation Co^{2+} (Fig. 1,*a*), Fe^{+2} (Fig. 1,*b*), Ni^{+2} (Fig. 1,*c*) or Cu^{+2} (Fig. 1,*d*) is 0.002 mol dm^{-3}. The reaction time is 1 h and 24 h.

The results evidence that all the complexes studied have the maximum *E* value at weakly acidic conditions. After the maximum, towards the neutral

solutions, E decreases and the time required for colour development increases due to the lack of nitrosating agent, HNO_2 (pK_a of HNO_2/NO_2^- is 3.37 [9]). Moreover, when pH is beyond 4, the solutions turn turbid because the cations or their complexes take an insoluble colloidal form. In more acidic solutions the complex formation after 1 h and 24 h coincide. Unfortunately, E is depressed in this region due to the competition between the cation added and proton for the place in the hydroxyl group of nitrosoalkylresorcinol.

As the E values for the cobalt and iron complexes are proved to be much higher than those for nickel and copper, the next regularities are described for the iron and cobalt cations only.
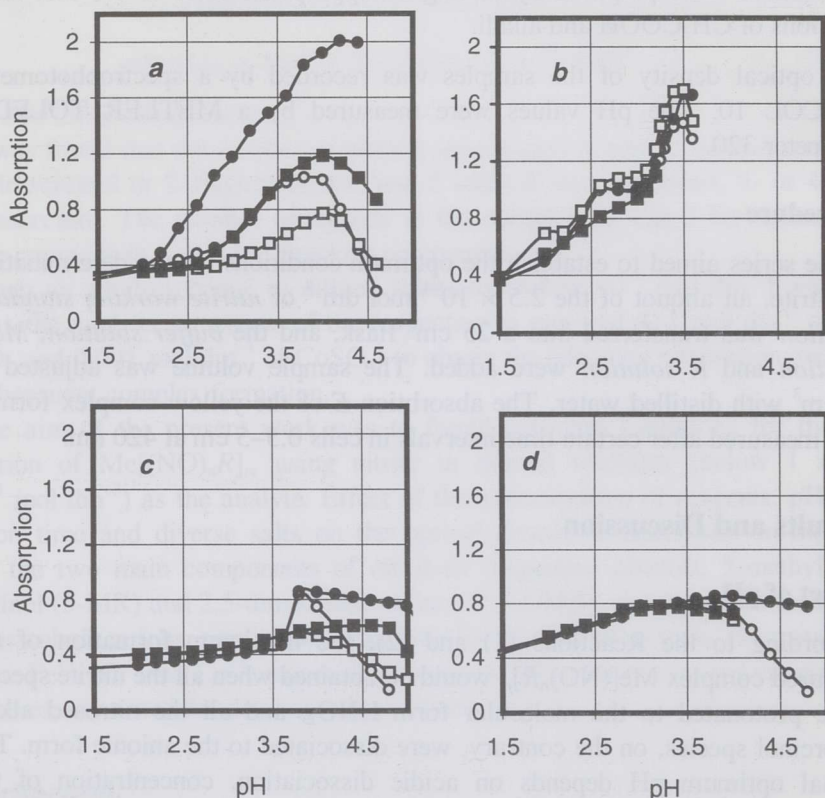

Fig. 1. Plot of absorption versus pH for cobalt (*a*), iron (*b*), nickel (*c*) and copper (*d*) complex: $[NO_2^-] = 5 \times 10^{-5}$ mol dm^{-3}; $[Me^{2+}] = 0.002$ mol dm^{-3}; $[R] = 0.01$ mol dm^{-3}; ● – 5-MR, 24 h; o – 5-MR, 1 h; ■ – 2,5-DMR, 24 h; □ – 2,5-DMR, 1 h

Effect of Alkylresorcinol Concentration

It is understandable that an excess of R is required for completion of the nitrosation process in diluted nitrite solutions. In this case the steady state for E can be achieved only when the sufficiently high concentration of alkylresor-

cinol ensures (i) utilization of all the nitrite (5×10^{-5} mol dm^{-3} in this series) for nitrosation of R according to the Reaction (1), (ii) rate-limiting kinetics of the Reaction (2) for the consequent reactions.
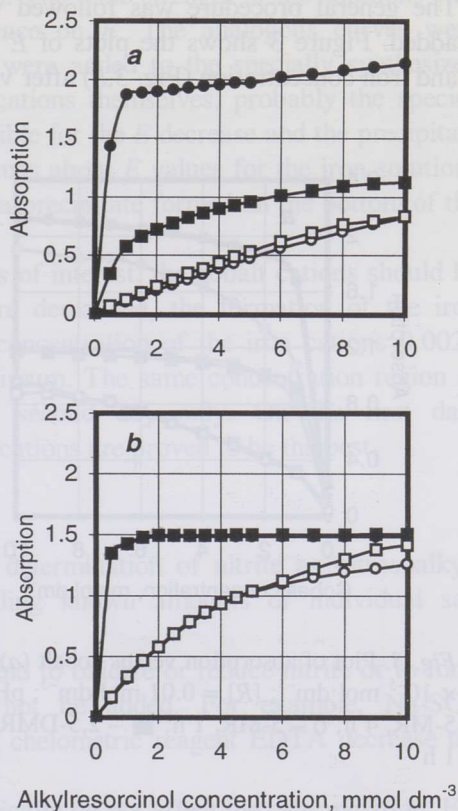

Fig. 2. Plot of absorption versus alkylresorcinol concentration for cobalt (*a*) and iron (*b*) complex: [NO$_2^-$] = 5×10^{-5} mol dm^{-3}; [Me^{2+}] = 0.002 mol dm^{-3}; pH$_{Co}$ = 4, pH$_{Fe}$ = 3.5; ● – 5-MR, 24 h; o – 5-MR, 1 h; ■ – 2,5-DMR, 24 h; □ – 2,5-DMR, 1 h

Figure 2 shows the plots of E versus 5-MR and 2,5-DMR concentration for cobalt (Fig. 2,*a*) and iron (Fig. 2,*b*) complexes after the reaction time 1 h and 24 h.

When the reaction time is 1 h, the steady state is not attained in the region of alkylresorcinol concentrations tested. In this case the complexes with nitroso-2,5-DMR and nitroso-5-MR ligands have the close E values.

When the reaction time is 22 h, the cobalt complex with 5-MR gives a colloidal suspension which has higher absorption than the complex with 2,5-DMR. For the iron complexes absorption with 5-MR and 2,5-DMR coincide.

The results evidence that 0.01 mol dm^{-3} of 5-MR or 2,5-DMR can be applied equally when the reaction time is some hours. When the aim is to obtain the highest sensitivity, 5-MR should be preferred and the reaction time

should be prolonged for the next day enabling to decrease the alkylresorcinol concentration to 0.001 mol dm^{-3}.

Effect of Cation Concentration

The general procedure was followed varying the amount of Me^{2+} solution added. Figure 3 shows the plots of E versus cobalt concentration (Fig. 3,a) and iron concentration (Fig. 3,b) after various hours.
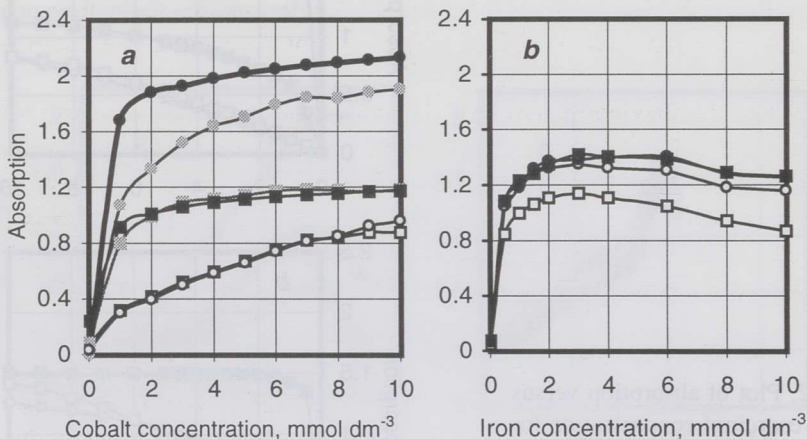

Fig. 3. Plot of absorption versus cobalt (a) and iron (b) concentration: $[NO_2^-] = 5 \times 10^{-5}$ mol dm^{-3}; $[R] = 0.01$ mol dm^{-3}; pH$_{Co}$ = 4; pH$_{Fe}$ = 3.5; ● – 5-MR, 24 h; ◉ – 5-MR, 4 h; o – 5-MR, 1 h; ■ – 2,5-DMR, 6 h; ▦ – 2,5-DMR, 4 h; □ – 2,5-DMR, 1 h

At zero concentration of the metal cations, the absorption $E(0)$ results from the formation of coloured 4-nitroso-5-methylresorcinol or 4-nitroso-2,5-dimethylresorcinol in these series. A decrease of $E(0)$ in time proves the unstability of the nitrosocompound without complex formation. Moreover, $E(0)$ depends on the ratio of the molar and anionic species of nitrosoalkylresorcinols.

The curves in Fig. 3 evidence that the type of chelating cation and alkylresorcinol, their concentration and the reaction time as well, have an essential influence on the E value. So, both the complex stability and formation kinetics are important characteristics of the process.

As expected, E of the cobalt complexes increases with an increase of cobalt concentration. So far as this effect is stronger at the first hours of the reaction, the consequence of the complex formation rate with cobalt cations is evident. On the second day of the reaction, E of the complexes with 5-MR reaches about twice higher values than on the first day. For the complexes with 2,5-DMR, the E values after 4 h and 24 h practically coincide.

E of the iron solutions attains its maximum value in the region of iron concentration 0.002–0.004 mol dm^{-3} during the first 1–4 hours and then decreases. To explain the unpredicted decrease in the E values at higher iron concentration and reaction time, pH of the solutions were checked and proved to be in the required ranges, 3.5–3.6. The ionic strength of the solutions was proved to have a negligible influence on E. The analogous curves were obtained when the iron(II) cations were added to the specially synthesized NO-5-MR solutions. So, the iron cations themselves, probably the species oxidized to Fe^{+3}, seem to be responsible for the E decrease and the precipitate formation. There is no sense to discuss about E values for the iron solutions measured on the second day due to a precipitate formed on the bottom of the flasks.

When the maximum sensitivity is of interest, the cobalt cations should be applied. When the quick results are demanded, the formation of the iron complex would be preferred. The concentration of the iron cations 0.002–0.004 mol dm^{-3} is suggested as optimum. The same concentration region of cobalt cations is enough on the second day only. On the first day, 0.01 mol dm^{-3} or more of the cobalt cations are proved to be the best.

Effect of Diverse Salts

The effect of diverse salts on the determination of nitrite as nitrosoalkyl-resorcinolates was studied by adding known amounts of individual salt solutions to a nitrite solution.

Naturally, the reagents, which tend to oxidize or reduce nitrite or to form stable cobalt complexes, should not be added. For example, Na$_2$SO$_3$, Na$_2$S$_2$O$_3$, FeCl$_3$ and widely applied chelometric reagent EDTA decrease the results seriously.

Most of the salts examined practically do not affect the determination. For example, when the concentration of nitrite in the test solution is 0.7 mg dm^{-3} of N-NO$_2^-$, 1000 mg dm^{-3} of NH$_4$Cl, NaCl, KCl, CaCl$_2$, AlCl$_3$, CoCl$_2$, Na$_2$SO$_4$, MgSO$_4$, NiSO$_4$, Cd(CH$_3$COO)$_2$ or Zn(CH$_3$COO)$_2$ practically does not interfere.

Since cadmium and ammonium cations were proved not to interfere, the method should be applied for determination of nitrate after its reduction by passing the sample through the Cd-Cu reduction column.

Procedure for Determination of Nitrite

Considering the influence of the factors studied, the following simple procedure is proposed for determination of nitrite:
- pipet V ml of a sample to a beaker
- add 0.25V ml of *Reagent*
- measure the absorption at 420 nm

Reagent contains:
1) 0.05 mol dm^{-3} of CoSO$_4$ or 0.01 mol dm^{-3} of FeSO$_4$
2) 0.05 mol dm^{-3} of 5-MR or 2,5-DMR
3) 0.5 mol dm^{-3} of acetic acid and KOH or NaOH added up to pH 4 when cobalt complex is formed, and up to pH 3.5 when iron complex is formed

Calibration Curves

Calibration curves were prepared by adding 5.0 cm^3 of cobalt or iron *Reagent Solution* to 20.0 cm^3 of the series of nitrite standard solutions.

Figure 4 shows the plot of optical density versus nitrite concentration range 0–1 mg dm^{-3} measured at 420 nm in 5-cm cells when 5-MR and cobalt or iron cations were added.
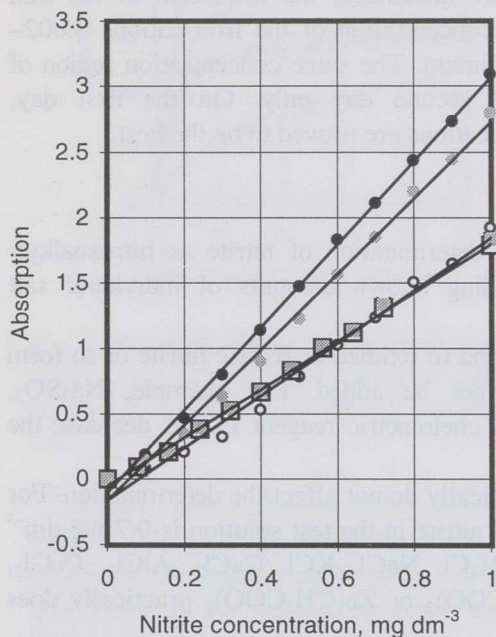

Fig. 4. Calibration curves for nitrite as cobalt or iron nitroso-5-methylresorcinolate [5-MR] = 0.01 mol dm^{-3}; [Me^{2+}] = 0.01 mol dm^{-3}; pH$_{Co}$ = 4; pH$_{Fe}$ = 3.5; o – Co, 1 h; ◉ – Co, 4 h; ● – Co, 24 h; □ – Fe ,1 h; ▨ – Fe, 4 h

Slopes of the curves for iron complex obtained after 1 h and 4 h practically coincide. The curves can be approximated to the linear trade lines shown in Fig. 4.

The slope for cobalt complex is close to that for iron complex when the reaction time is 1 h. However, the slope for cobalt curves increases significantly in time. The steady state is attained only on the second day. Nevertheless, the adequate test results can be obtained before the reaction equilibrium when the same concentration of the reagents and the same reaction time are applied for nitrite samples and standard solutions.

The constants of the approximated linear relationships for the curves in Fig. 4, and for an order higher concentration range of nitrite, 0–10 mg dm^{-3}, are given in the Table.

Characteristics of Calibration Curves

C, mg dm^{-3}	Reaction time h	Cell length, mm	n	r	a	b	C_{min}, mg/dm^3
		Cation Fe					
0.1–1	1	50	11	0.985	–0.10	2.06	0.10
0.1–1	4	50	11	0.985	–0.06	2.02	0.06
1–10	1	5	9	0.999	–0.009	0.1876	0.10
		Cation Co					
0.1–1	1	50	14	0.998	–0.37	2.29	0.32
0.1–1	4	50	14	0.998	–0.36	3.16	0.23
0.1–1	24	50	14	0.999	–0.19	3.28	0.12

C – N-NO$_2^-$ concentration range in standard solutions; n – number of experimental points, r – correlation coefficient.

It is noteworthy that every curve in Fig. 4 begins with a concave part resulted from the uncompleted nitrosation and slow complex formation at low nitrite concentrations. The minimum concentration of nitrite being found by the linear regression

$$C = a + bE \text{ (mg dm}^{-3})$$

can be described by the equation

$$C_{min} = -2a/b$$

The Table demonstrates that the absolute value of the regression constant term a decreases and coefficient b increases with completion of the complex formation. Subsequently, C_{min} decreases in time. Moreover, though the apparent specific absorption of cobalt complex is higher than of iron complex, the value for C_{min} is lower for iron complex. This can be explained by the second- and third-order effect of ligand concentration at formation of Fe(NO-C$_6$H$_2$OHO)$_2$ and Co(NO–C$_6$H$_2$OHO)$_3$.

Conclusions

A new colorimetric method for determination of nitrite as a cobalt or iron complex of nitrosed alkylresorcinol is proposed. The method is simpler and less toxic than the standard diazotation-coupling test method and applies the dihydric phenols produced by dephenolation of oil shale semicocking waters as effective reagents.

A disadvantage of the method is slow formation of the complex. Nevertheless, when the test conditions are constant, the linearity of calibration curves is obeyed in the concentration region 0.1–10 mg/dm^3.

Acknowledgements

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