

## Spectrophotometric Determinations of 2-Nitroso-1-naphthol

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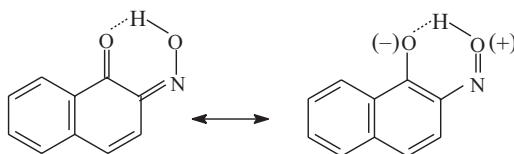
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Determinations of micro amounts of 2-nitroso-1-naphthol were performed by measuring its proper absorptions in the UV-Vis spectral region in ethanol and in acidic and basic ethanol-water solutions. Further, a procedure of determining 2-nitroso-1-naphthol, based on its reaction with the  $\text{Fe}^{2+}$  ion, is proposed.

*Key words:* 2-nitroso-1-naphthol, Mohr's salt, UV-Vis spectrophotometry.

### INTRODUCTION

*Ortho*-substituted nitronaphthols can undergo tautomerisation to give oxo-oximes. In the case of 2-nitroso-1-naphthol, the equilibrium is greatly displaced toward the keto-form and the compound has, in the solid state and in solution, a predominately quinone oximic structure,<sup>1–6</sup> which is a hybrid of resonance forms of the type:



2-Nitroso-1-naphthol is currently used as a complexing agent in the analysis of cobalt<sup>7,8</sup> and it is also a sensitive and specific reagent for fluori-

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metric determinations of tyrosine residues in proteins and peptides.<sup>9</sup> Like other phenols and naphthols, it belongs to biologically important compounds, especially because of its cytotoxic action.<sup>10</sup> It makes part of noxious substances in the industry of polymers, cosmetic and pharmaceutical preparations, dyes and pesticides.<sup>11</sup> Hence, the methods of determining 2-nitroso-1-naphthol may be of practical importance.

To date, only one method of determining 2-nitroso-1-naphthol has been described in the literature, within a set of procedures developed for photometric determinations of naphthols and their derivatives in aqueous media.<sup>11</sup> It was suggested for routine analysis of the total and individual nitroso-naphthol content in waste waters at hazardous concentration levels. Samples were previously acidified (pH = 2–3) and preconcentrated by extraction with equimolar portions of nonane and tributylphosphate. The yellow coloured extracts were then treated with anhydrous sodium sulphate and their absorbance measured at 400 nm. Rather scarce analytically relevant data were quoted, so the performed work does not appear quite clear.

During our investigations of cyanoferrate complexes of nitrosonaphthols we encountered the necessity of determining 2-nitroso-1-naphthol. First, we examined the possibility of determining 2-nitroso-1-naphthol by measuring its proper absorptions in the UV-Vis region (Procedures A, B and C). Second, an additional simple method of determining 2-nitroso-1-naphthol based on its reaction with the  $\text{Fe}^{2+}$  ion was developed (Procedure D). The results of these examinations are reported in this paper.

## EXPERIMENTAL

All chemicals used were of analytical reagent grade. 2-Nitroso-1-naphthol was a Fluka Chemie (Buchs, Switzerland) reagent, further purified by recrystallisation from a water-ethanol mixture (m.p. 142–144 °C) and its solutions were prepared in absolute ethanol. Mohr's salt,  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6 \text{H}_2\text{O}$ , was a product of Kemika (Zagreb, Croatia) and was used as supplied. Britton-Robinson buffers were prepared by mixing 100 mL of phosphoric, boric and acetic acid mixtures (all  $0.04 \text{ mol dm}^{-3}$ ) with different volumes of  $0.2 \text{ mol dm}^{-3}$  sodium hydroxide. The constant ionic strength of  $0.05 \text{ mol dm}^{-3}$  was maintained with sodium chloride.

Spectrophotometrical measurements were performed with UNICAM UV-Vis spectrophotometer UV4-100 and 1-cm silica-glass cells. Preliminary examinations were made with UNICAM SP600 UV spectrophotometer.

### *Procedures*

A. – 1 mL of a standard solution containing 1–50  $\mu\text{g}$  of 2-nitroso-1-naphthol was diluted with absolute ethanol up to 5 mL. The absorbance was measured against water at 261 nm.

B. – To 1 mL of a standard solution containing 1–50  $\mu\text{g}$  of 2-nitroso-1-naphthol, 2.5 mL of 0.1 mol  $\text{dm}^{-3}$  HCl was added and diluted with water up to 5 mL. The resulting 20% (volume fraction,  $\phi$ ) ethanol-water solution was mixed and its absorbance measured against water at 261 nm.

C. – The same procedure as in B was followed using 0.1 mol  $\text{dm}^{-3}$  NaOH, except for the solutions containing 5–50  $\mu\text{g}$  of 2-nitroso-1-naphthol and the absorbances measured at 278, 325 and 430 nm.

D. – To 2 mL of the Britton-Robinson buffer of pH = 6.06, 1 mL of a standard solution containing 10–100  $\mu\text{g}$  of 2-nitroso-1-naphthol was added, followed by addition of 1 mL of the reagent solution ( $c(\text{Fe}^{2+}) = 0.001 \text{ mol dm}^{-3}$ ) and water up to 5 mL. The mixtures were shaken and their absorbances were measured within 2–3 minutes at  $\lambda_{\text{m}} = 700 \text{ nm}$  against water.

## RESULTS AND DISCUSSION

2-Nitroso-1-naphthol is a yellow powder sparingly soluble in water. Its UV-Vis spectrum in ethanol has been recorded earlier<sup>4</sup> and shows three absorption maxima, the highest at 261 nm and two much weaker at about 303 and 416 nm. It was found during this work that the maxima are pronouncedly pH-dependent in ethanol-water solutions (Figure 1). The only high absorption in acidic media situated at 261 nm ( $\epsilon = 26825 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$  at pH from 1 to 5) as well as the maximum at 278 nm in neutral and basic media ( $\epsilon = 14500 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$  at pH over 12) are due to  $\pi \rightarrow \pi^*$  transitions within the *ortho*-quinone oxime system, while the maxima centered around 340 nm in acidic media ( $\epsilon = 3900 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$  at pH from 1 to 5) and 325 nm in neutral and basic media ( $\epsilon = 9580 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$  at pH over 12) are characteristic of *o*-benzoquinones.<sup>1</sup> The absorptions around 400 and 430 nm ( $\epsilon = 3500 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$  at pH from 1 to 5 and  $\epsilon = 9800 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$  at pH over 12), present also in the spectrum of 1-nitroso-2-naphthol,<sup>2</sup> are associated with the intramolecular ligand's charge resonance.

Determinations of 2-nitroso-1-naphthol were undertaken by measuring its proper absorption at 261 nm in ethanol and in acidic ( $c_{\text{HCl}} = 0.05 \text{ mol dm}^{-3}$ ) ethanol-water solutions as well as by measuring the absorbances at 278, 325 and 430 nm of alkaline ( $c_{\text{NaOH}} = 0.05 \text{ mol dm}^{-3}$ ) ethanol-water solutions. The validity of Beer's law was examined over the range of 1–50  $\mu\text{g}$  / 5 mL of solutions for procedures A and B and of 5–50  $\mu\text{g}$  / 5 mL of solutions for procedure C, and it was found to be obeyed. The results of these determinations are presented in Table I.

An additional simple method of determining 2-nitroso-1-naphthol is proposed, based on its reaction with the  $\text{Fe}^{2+}$  ion.

2-Nitroso-1-naphthol is known to react with the  $\text{Fe}^{2+}$  ion by forming in a few minutes a green coloured complex, which then begins to disintegrate

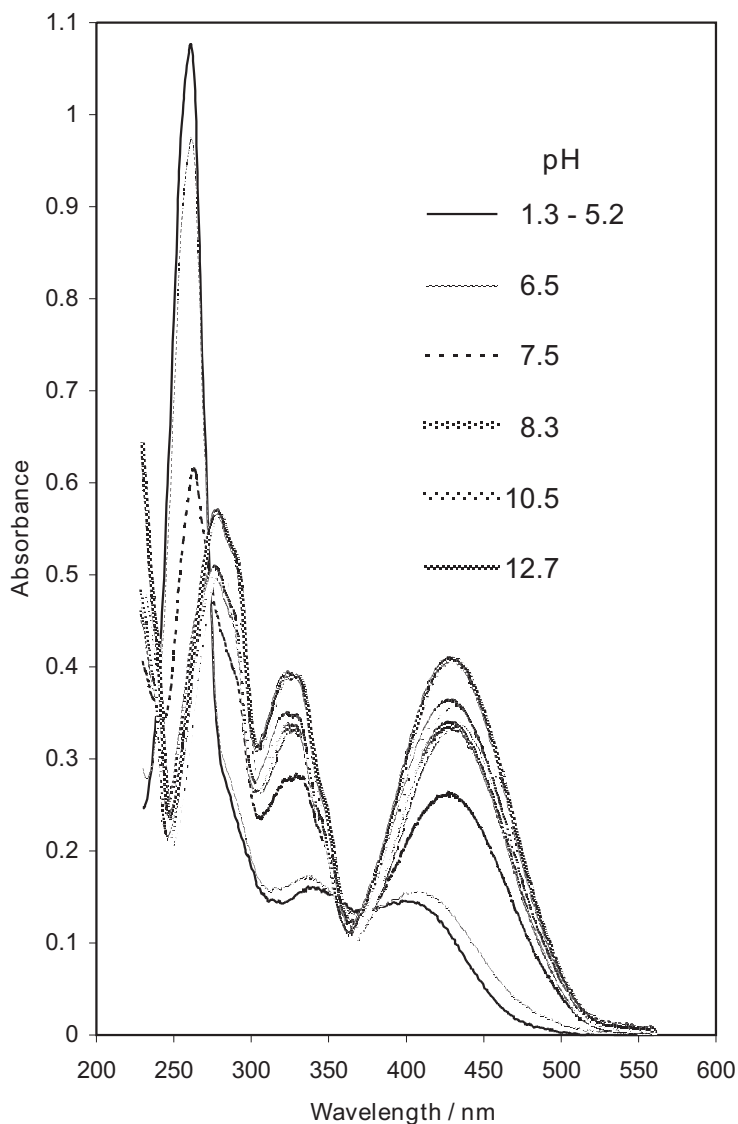


Figure 1. UV-Vis spectra of solutions of 2-nitroso-1-naphthol (ethanol-water; volume fraction of ethanol,  $\phi = 20\%$ ) in different pH media at 25 °C.  $I = 0.05 \text{ mol dm}^{-3}$ ;  $c = 4 \times 10^{-5} \text{ mol dm}^{-3}$ .

(Figure 2). The characteristics of the complex and the optimum conditions for its formation have been described.<sup>12,13</sup> It is the tris(2-nitroso-1-naphtholato)ferrate(II) ion, ( $\lambda_m = 700 \text{ nm}$ ,  $K_{\text{stability}} = 7.58 \times 10^{13} \text{ mol}^{-3} \text{ dm}^9$  (24 °C),  $\epsilon = 23400 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ )<sup>12,13</sup> where the ligand is bound to iron as an anionic

TABLE I

Determination of 2-nitroso-1-naphthol by measuring its proper absorptions in ethanol (A) and in acidic (B) and basic (C) ethanol-water solutions (ethanol,  $\phi = 20\%$ ) within 24 hours

Procedure	Media	$\lambda_m$ nm	Taken $\mu\text{g}$	A	Found $\mu\text{g}$	S.D.	R.S.D. %	No. of detns.
A	ethanol	261	1	0.036	1.20	0.04	2.96	5
			10	0.310	9.83	0.12	1.19	5
			40	1.266	40.01	0.30	0.76	5
$y = 0.0317x - 0.002; r = 0.9995$								
B	0.05 mol dm <sup>-3</sup> HCl	261	1	0.031	0.93	0.04	4.81	5
			10	0.334	9.96	0.04	0.42	5
			40	1.347	40.11	0.11	0.28	5
$y = 0.0336x - 0.0004; r = 0.9998$								
C	0.05 mol dm <sup>-3</sup> NaOH	325	5	0.097	4.95	0.06	1.24	5
			10	0.182	9.98	0.28	2.80	5
			40	0.686	39.83	0.21	0.54	5
$y = 0.0169x + 0.0131; r = 0.9990$								
C	0.05 mol dm <sup>-3</sup> NaOH	325	5	0.069	4.90	0.06	1.25	5
			10	0.132	9.90	0.35	3.57	5
			40	0.503	39.82	0.23	0.58	5
$y = 0.0124x + 0.0089; r = 0.9991$								
C	0.05 mol dm <sup>-3</sup> NaOH	430	5	0.082	5.00	0.03	0.54	5
			10	0.158	10.01	0.04	0.42	5
			40	0.616	40.10	0.08	0.20	5
$y = 0.0152x + 0.0064; r = 0.9990$								

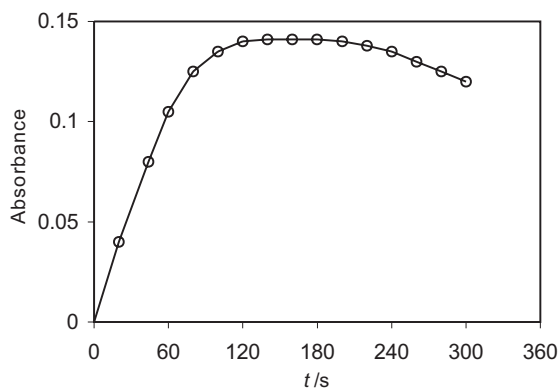


Figure 2. Variation of the absorbance of the tris(2-nitroso-1-naphtholato)ferrate(II) complex ( $\lambda_m = 700$  nm) as a function of time at 25 °C.  $I = 0.05$  mol dm<sup>-3</sup>, pH = 6.06,  $c(\text{reagent}) = 2 \times 10^{-4}$  mol dm<sup>-3</sup>,  $c(2\text{-nitroso-1-naphthol}) = 2.3 \times 10^{-5}$  mol dm<sup>-3</sup>.

moiety, which is similar to other metal chelates of 2-nitroso-1-naphthol.<sup>7</sup> The high charge-transfer band appearing in the visible region upon complex formation allowed to develop a new spectrophotometric procedure of determining small quantities of 2-nitroso-1-naphthol in ethanol-water solutions. The optimum content of ethanol present in the reaction mixture is 10–30% ( $\phi$ ) ethanol-water. Higher and lower contents of ethanol decrease the absorbance (Figure 3). The concentration ratio of the reagent toward the 2-nitroso-1-

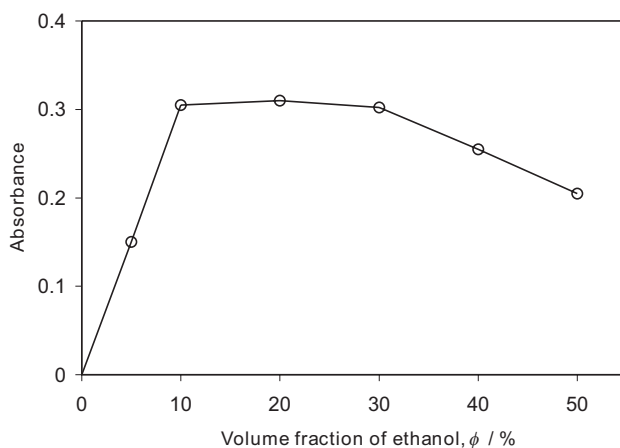


Figure 3. Dependence of the absorbances of the tris(2-nitroso-1-naphtholato)ferrate(II) complex ( $\lambda_m = 700$  nm) on the volume fraction of ethanol in water-ethanol buffered solutions at 25 °C.  $I = 0.05$  mol dm<sup>-3</sup>, pH = 6.06,  $c(\text{reagent}) = 2 \times 10^{-4}$  mol dm<sup>-3</sup>,  $c(2\text{-nitroso-1-naphthol}) = 5 \times 10^{-5}$  mol dm<sup>-3</sup>. Absorbances were measured against water within 2.5 minutes.

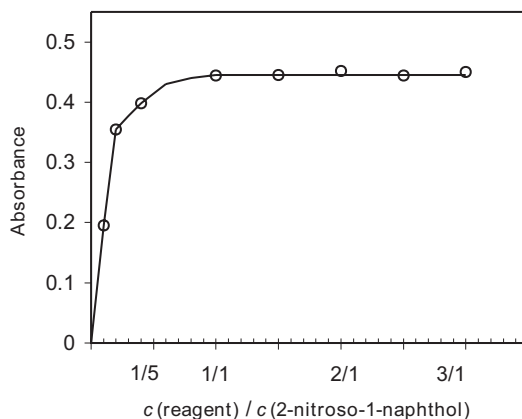


Figure 4. Dependence of absorbance values of the tris(2-nitroso-1-naphtholato)ferrate(II) complex ( $\lambda_m = 700$  nm) on the molar ratio of reactants at 25 °C.  $I = 0.05$  mol dm<sup>-3</sup>, pH = 6.06,  $c(2\text{-nitroso-1-naphthol}) = 8 \times 10^{-5}$  mol dm<sup>-3</sup>.

naphthol must be at least 1:1 to ensure the independence of the absorbance value from the mole ratio of the reactants (Figure 4). Beer's law is obeyed up to an absorbance of about 1.6 (200  $\mu\text{g}$ ). The actual results and the linear concentration-absorbance relationship obtained by regression are presented in Table II.

Species reacting with the Fe<sup>2+</sup> ion or 2-nitroso-1-naphthol under the conditions used will interfere with all the proposed procedures. So did 1-nitroso-2-naphthol, the nitroso-R-salt and the Co<sup>2+</sup> and Pd<sup>2+</sup> ions.

A 100-fold amount ( $w$ ) of phenol and  $\alpha$ - and  $\beta$ -naphthols as well as a pure bovine albumin and human blood serum up to a 10-fold excess did not interfere with the method of complexing 2-nitroso-1-naphthol by iron(II) ions, but interfered with the determinations in the UV-Vis region.

The actual results offer evidence of the possibility of determining 2-nitroso-1-naphthol in ethanol and ethanol-water solutions.

TABLE II  
Determination of 2-nitroso-1-naphthol with Mohr's salt

Taken / $\mu\text{g}$	A	Found <sup>a</sup> / $\mu\text{g}$	S.D.	R.S.D. / %	No. of detns.
10	0.075	11.3	0.3	3.2	5
50	0.382	50.7	0.4	0.7	5
100	0.773	100.8	0.8	0.8	5

<sup>a</sup> Calculated by means of the calibration equation:  $y = 0.0078x - 0.0135$ ;  $r = 0.9997$ ;  $x$  is expressed in  $\mu\text{g}/5$  mL of the reaction mixture.

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## SAŽETAK

## Spektrofotometrijska određivanja 2-nitrozo-1-naftola

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Određivanje mikrokoličina 2-nitrozo-1-naftola u etanolu te u kiselim i baznim etanol-vodenim otopinama izvedeno je mjerenjem njegovih karakterističnih apsorpcija u UV-Vis spektralnom području. Predložena je i jednostavna metoda određivanja 2-nitrozo-1-naftola koja se temelji na njegovoj reakciji s ionima  $\text{Fe}^{2+}$ .