

# ON THE DIOXIMINE COMPLEXES OF TRANSITION METALS. PART XCIV. NEW RHODIUM(III) COMPLEXES WITH $\alpha$ -SUBSTITUTED ALIPHATIC AND ALICYCLIC OXIMES

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## Abstract

Some chelating agents were obtained by condensation of the  $\alpha$ -keto-oximes diacetylmonoxime, methyl-isopropyl-2,3-dione-monoxime (2) and 1,2,3-cyclohexane trione dioxime (1,3) with semicarbazide and thiosemicarbazide. The formation of rhodium(III) chelates with these reagents was studied spectrophotometrically in a wide pH-range using the continuous variation method.

Some derivatives were proposed for the analytical determination of this metal.

*Keywords:* rhodium complex, oxime, spectrophotometry.

## Introduction

Various oxime derivatives:  $\alpha$ -dioximes,  $\alpha$ -keto-oximes form coloured complexes with rhodium(III) in a wide pH range. Their colour varies from light yellow to dark brown depending on the molecular structure of the chelating agent, and for the anionic complexes (e. g.  $[\text{Rh}(\text{Diox.H})_2\text{X}_2]^-$ -Diox.H<sub>2</sub>- $\alpha$ -dioxime, X<sup>-</sup>-halide or pseudohalide) on the nature of the anion present. Some aliphatic  $\alpha$ -dioximes were used for the synthesis of  $[\text{Rh}(\text{Diox.H})_2\text{X}_2]^-$  type derivatives [1-3]. The kinetics and mechanism of the aquation of these compounds were studied by SYRZOVA et al. [4].

Among the  $\alpha$ -dioximes, the  $\alpha$ -keto-oximes present also chelating properties towards rhodium(III). From this class of combinations the  $\alpha$ -nitrozo- $\beta$ -naphthol [5], thiophene-2-aldoxime [6],  $\alpha$ -benzylmonoxime [7], phenanthrenequinone-monoxime [8] have been used for the spectrophotometric determination of the above-mentioned metal.

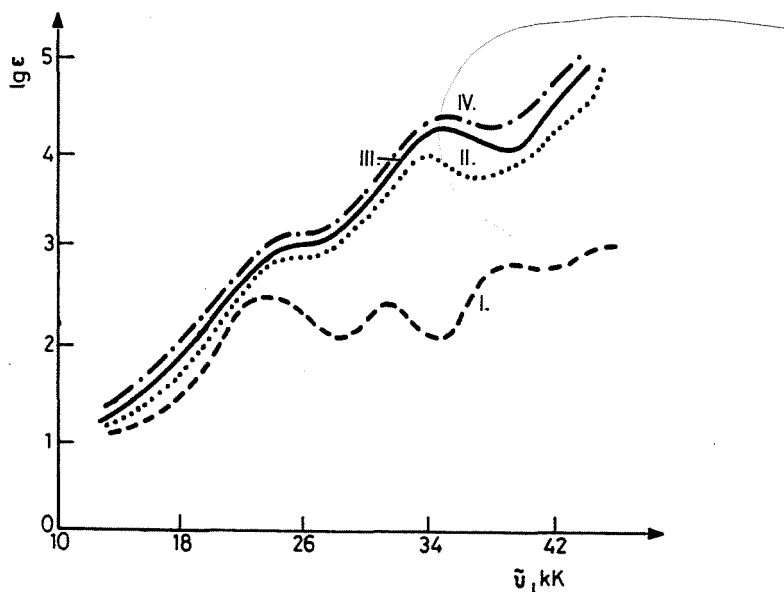
The majority of the condensation products of the  $\alpha$ -keto-oximes with semicarbazide, thiosemicarbazide, hydrazine, phenylhydrazine, etc. were not studied from this point of view.

In this paper the formation, optical properties and analytical applications of some rhodium(III) complexes with oxime- $\alpha$ -semicarbazones and oxime- $\alpha$ -thiosemicarbazones are presented.

## Results and Discussion

The electronic spectra of the  $\text{RhCl}_3$  - chelating agent systems were studied at various pH values in ethanol-water mixtures. In some cases (sparingly soluble reagents) 40 % ethanol, 40 % water, 20 % dimethylsulphoxide mixtures were also used.

The spectral data of the complexes studied are presented in *Table 1*. The electronic spectra are shown in *Figs. 1-4*.



*Fig. 1.* Electronic spectra of  $\text{RhCl}_3$  and of some  $\text{RhCl}_3$ -oxime systems; I.  $\text{RhCl}_3$ , II.  $\text{RhCl}_3$ -diacetylmonoxime-semicarbazone (pH=1.81). III. idem, pH=3.29 IV. idem, pH=7.96

In the case of the oxime chelates of rhodium(III) the absorption bands of  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  at 22 kK and 29 kK disappear and only a single band or

Table 1

Electronic spectral data for some Rh(III)-oxime systems at various pH values

Oxime	$\bar{\nu}_1$ (kK) log $\epsilon_1$	$\bar{\nu}_2$ (kK) log $\epsilon_2$	$\bar{\nu}_3$ (kK) log $\epsilon_3$
diacetylmonoxime			
pH = 1.81	25-27; 2.6	31-33 3.25	44.5 4.63
pH = 4.10	25-26; 3.1	31-33 3.5	44.5 4.5
dimethylglyoxime			
pH = 4.1	24-28 3.1	35-37 4.7	48 5.1
diacetylmonoxime-thiosemicarbazone			
pH = 1.81	22.5-24.2 2.9	33.5-34.2 4.45	48-48.5 4.9
pH = 3.29	22.5-24.8 3.0	33.7-34.8 4.60	47.8-4.8 4.9
pH = 7.96	22.2-24 2.95	33.9-35.0 4.60	48 4.9
diacetylmonoxime-semicarbazone			
pH = 1.81	24-27; 2.9	33.5-35 4.10	47 4.8
pH = 3.29	24-27; 3.1	33.5-35.5 4.20	47 4.9
pH = 7.96	24-25; 3.20	33.5-35.5 4.25	47 4.8
methyl-isopropyl-2,3-dione monoxime-thiosemicarbazone			
pH = 1.8	22-23.7 2.8	33-34.5 4.85	47.5 4.7
pH = 3.29	22-24.5 2.85	33-34.5 4.95	48 4.7
pH = 7.96	22-24.5; 2.80	33-35 5.10	48 4.75
1,2,3-cyclohexane trione dioxime(1,3)-semicarbazone			
pH = 1.81	22-24 2.5	29.5-32 3.2	47.5 4.5
pH = 3.29	22-24 2.45	29.5-32 3.2	47.5 4.5
pH = 7.96	22-24 2.40	29-32 2.85	47.5 4.5
1,2,3-cyclohexane trione dioxime (1,3)-thiosemicarbazone			
pH = 1.81	22-24 2.6	29-31 3.3	46-47 4.7
pH = 3.29	22-24.5 2.65	29-31 3.4	47 4.7

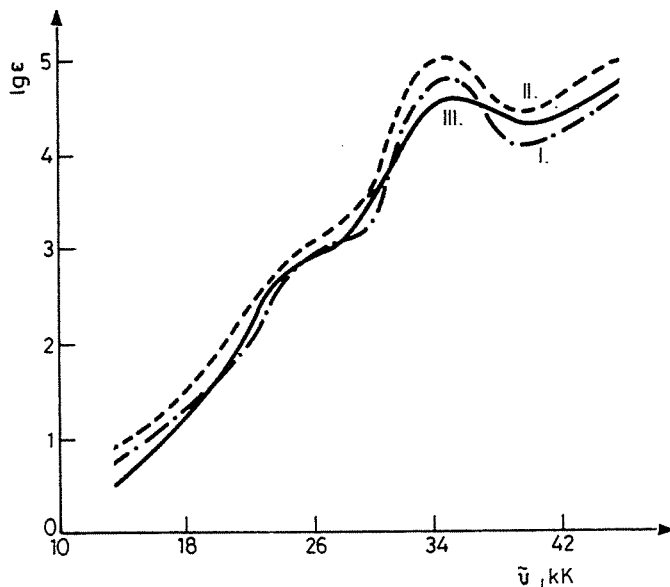


Fig. 2. Electronic spectra of some  $\text{RhCl}_3$ -diacetylmonoxime-thiosemicarbazone systems; I. pH=1.81, II. idem, pH=3.29, III. pH=7.96

inflection is present at 24–28 kK or at 25–30 kK, respectively, in the visible part of the spectrum, the position of which is influenced to some extent by the nature of the ligand (dioxime, keto-oxime, etc.).

The UV spectra of the  $[\text{Rh}(\text{Diox.H})_2\text{X}_2]^-$  complexes show an analogy with those of the  $[\text{Co}(\text{Diox.H})_2\text{X}_2]$  ones. This suggests an analogous trans-octahedral structure. The UV band at 40–41 kK appears in the spectra of all complexes of the  $[\text{Co}(\text{Diox.H})_2\text{XY}]$ ,  $[\text{Co}(\text{Diox.H})_2\text{XL}]$  types (L – neutral ligand) and can be attributed to the  $[\text{Co}(\text{Diox.H})_2]$  coplanar moiety [9]. By the substitution of the central cobalt atom by rhodium having a greater atomic number a hypsochromic effect occurs. Following this phenomenon the mentioned absorption band is shifted towards lower wave numbers: 35–37 kK. In the spectra of the Rh-keto-oxime, Rh- $\alpha$ -substituted oxime systems the band 35–37 kK is generally absent and a new band appears at 30–34 kK. This suggests the possible appearance of another geometric structure (asymmetric).

In the spectra of the above-mentioned complexes the band at 45–48 kK can be attributed to a charge transfer of the various oxime ligands.

Spectrophotometric studies on the  $\text{Rh}^{3+}$ - $\alpha$ -dioxime (aliphatic or alicyclic dioximes) systems show the formation of  $\text{Rh:L} = 1:2$  complexes.

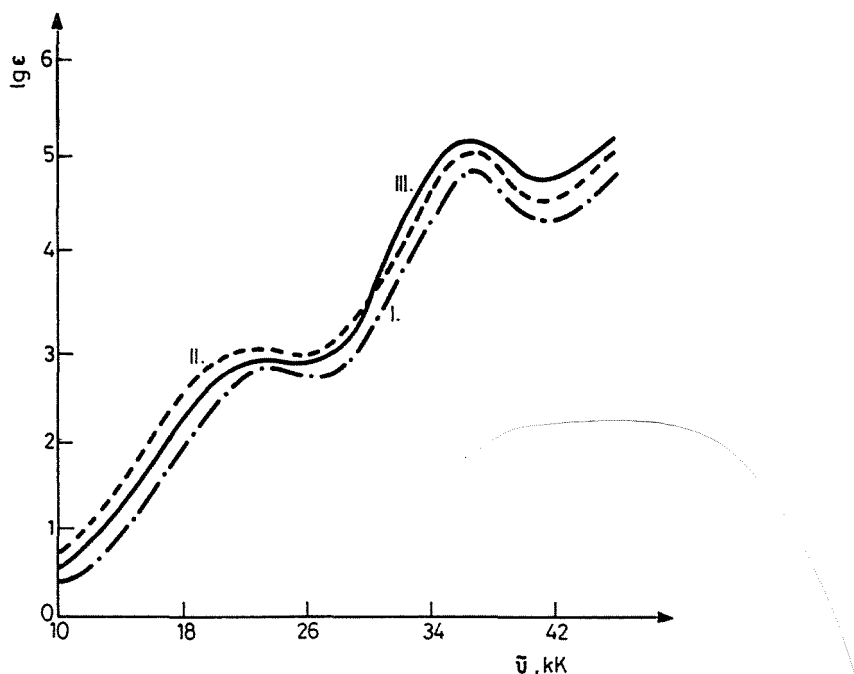


Fig. 3. Electronic spectra of some  $\text{RhCl}_3$ -methyl-isopropyl-2,3-dione-oxime-thiosemicarbazone systems; I. pH=1.81, II. idem, pH=3.29, III. idem pH=7.96

Using  $\alpha$ -keto-oximes for this study the formation of  $\text{Rh:L} = 1:3$  derivatives can be observed. Using the continuous variation method for the analogous  $\text{Co(III)}$ -keto-oxime systems, the formation of  $\text{Co:L} = 1:3$  chelates with asymmetric structure and a non-electrolytic character can be established [10].

The X-ray and IR measurements on some crystalline dimethyl-glyoximine chelates of rhodium:  $\text{H}[\text{Rh}(\text{DH})_2\text{Cl}_2]$ ,  $\text{H}[\text{Rh}(\text{DH})_2\text{Br}_2]$ , show that these types of complexes have a symmetric trans geometric configuration stabilized by short intramolecular  $\text{O-H} \dots \text{O}$  hydrogen bridges [11, 12].

The continuous variation curves (Fig. 5) of the Rh-oxime-thiosemicarbazone and Rh-oxime-thiosemicarbazone systems at lower pH-values (1.81, 2.50), unlike the Rh- $\alpha$ -dioxime (1:2) and Rh- $\alpha$ -ketoxime (1:3) complexes show the formation of  $\text{Rh} : \text{oxime} = 1:1$  derivatives. The UV spectral data present also important deviations from those of the former (Table 1).

It was observed that at higher pH values and in the presence of an excess of  $\text{Rh}^{3+}$  ( $\text{Rh}^{3+}/\text{L} > 1$ ), the solutions become turbid because of the formation of  $\text{Rh}(\text{OH})_3$  or some hydroxo-complexes.

The Job's curves of these systems at 440 and 480 nm, at various pH values are shown in Figs. 6-8.

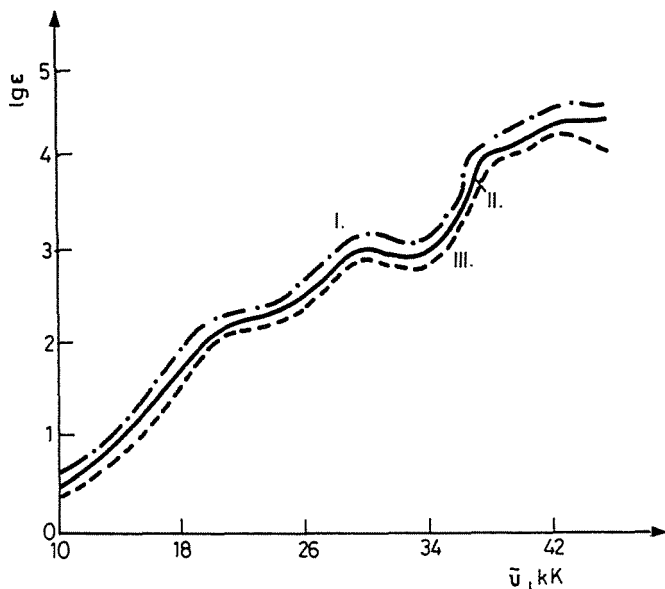


Fig. 4. Electronic spectra of some  $\text{RhCl}_3$ -1,2,3-cyclohexane trione dioxime (1,3)-semicarbazone (2); I. pH=1.81, II. idem, pH=3.29, III. idem pH=7.96

The geometric structures of the Rh : oxime = 1:2, 1:3 and 1:1 derivatives are presented in Fig. 9.

The trans, symmetric octahedral arrangement of  $[\text{Rh}(\text{Diox.H})_2\text{X}_2]^-$  is shown in Fig. 9a. In the case of  $\alpha$ -keto-oximes the bidentate ligands take part in the formation of an octahedral asymmetric structure (Fig. 9b). The tridentate oxime-semicarbazone and oxime thiosemicarbazone ligands form, probably, five and six membered rings with the metal ion (Fig. 9c). These chelates have an ionic character and cannot be extracted from aqueous-alcoholic media with apolar solvents (benzene,  $\text{CCl}_4$ ).

As compared with the analogous Co(III) and Cu(II) complexes (yellow-brown, green), the rate of formation of these derivatives is 100–1000 times slower and for this reason it is necessary to heat the samples in aqueous-alcoholic solutions (45–60 minutes on a sand (oil) bath).

The yellow-brown solutions follow Beer's law in a wide concentration range ( $5 \times 10^{-5}$ – $10^{-3}$  mol/l Rh) (Fig. 10). The sensitivity of these colour reactions is, however, not very high ( $\epsilon = 500$ – $3000$ ) in the visible region.

The intensity of the colour becomes constant after 25–30 minutes and does not change up to 24–36 hours (Fig. 11).

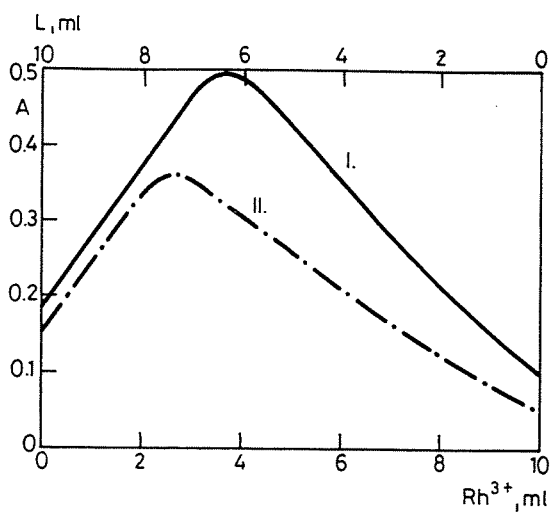


Fig. 5. Continuous variation curves of  
 I.  $\text{RhCl}_3$ -methyl-isopropyl-2,3-dione-dioxime systems;  $\text{pH}=1.81$   
 II.  $\text{RhCl}_3$ -methyl-isopropyl-2,3-dione-monoxime (3) systems;  $\text{pH}=1.81$

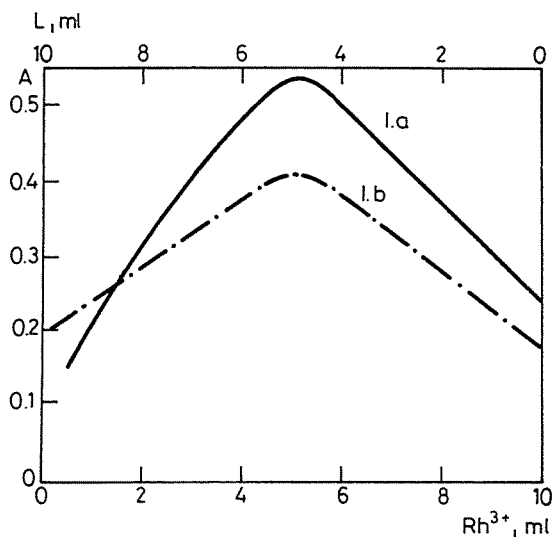


Fig. 6. Continuous variation curves of  
 I. a.  $\text{RhCl}_3$ -diacetylmonoxime-semicarbazone systems;  $\text{pH}=1.81$ , 440 nm  
 I. b.  $\text{pH}=1.81$ , 480 nm

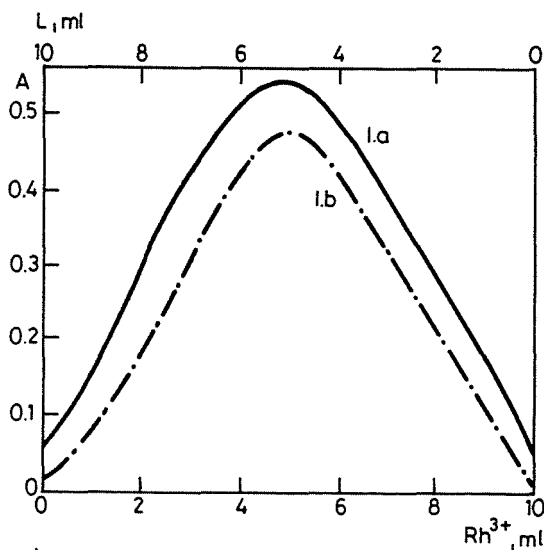


Fig. 7. Continuous variation curves of  
 I. a.  $\text{RhCl}_3$ -diacetylmonoxime-thiosemicarbazone systems; pH=1.81, 440 nm  
 I. b. pH=1.81, 480 nm

With the exception of iridium, the other platinumic metals, which form sparingly soluble complexes with oxime derivatives (Pt, Pd) do not interfere with the spectrophotometric determination of rhodium. The interference by Ru and Os was not studied. Cu and Co have to be absent since they also form coloured, soluble compounds with these oxime derivatives.

### Experimental

The oxime- $\alpha$ -semicarbazone and oxime- $\alpha$ -thiosemicarbazone derivatives were obtained by condensation of diacetylmonoxime, methyl-isopropyl-2,3-dione-monoxime (3), 1,2,3-cyclohexane trione-dioxime (1,3) [13] with semicarbazide (hydrochloride) and thiosemicarbazide, respectively, at room temperature, in aqueous-alcoholic solutions during 48 hours. The crude products were recrystallized.



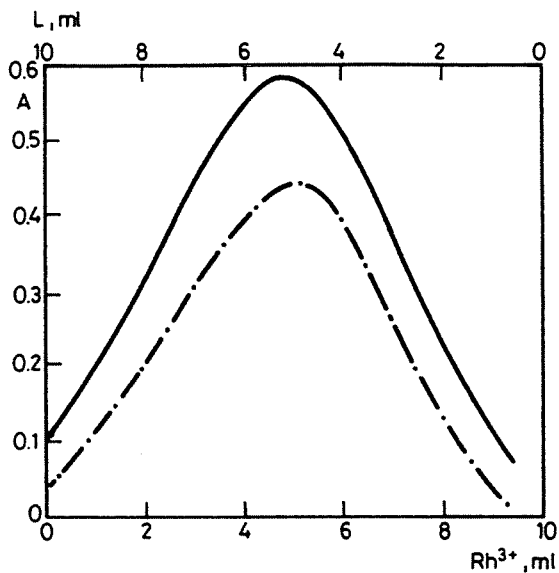


Fig. 8. Continuous variation curves of  
 I. a.  $\text{RhCl}_3$ -1,2,3-cyclohexane trione dioxime (1,3)-thiosemicarbazone (2) systems;  $\text{pH}=1.81$ , 440 nm  
 I. b.  $\text{pH}=1.81$ , 480 nm

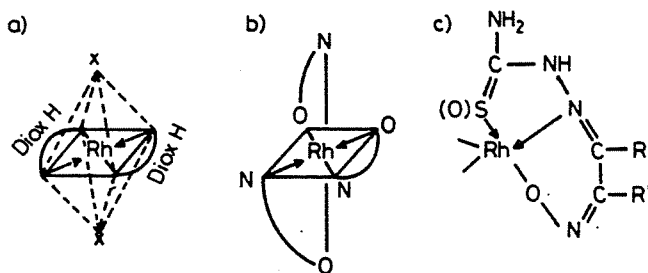


Fig. 9. Geometric structure of the Rh: oxime 1:2, 1:3 and 1:1 complexes  
 9a —  $[\text{Rh}(\text{Diox.H})_2\text{X}_2]^-$   
 9b —  $[\text{Rh}(\text{Ketoxime})_3]$   
 9c —  $\text{Rh}(\text{oxime-}\alpha\text{-thiosemicarbazone})$

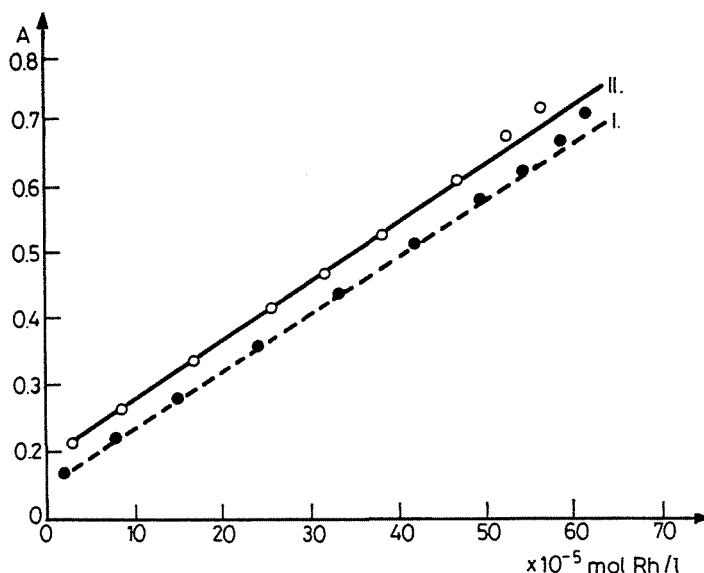


Fig. 10. Validity of Beer's law for  
 I. the  $\text{RhCl}_3$ -methyl-isopropyl-2,3-dione-oxime-thiosemicarbazone system  
 II. the  $\text{RhCl}_3$ -1,2,3-cyclohexane trione-dioxime (1,3)-thiosemicarbazone system

#### *General Procedure for the Spectrophotometric Determination of Rh(III)*

The samples containing 0.01–1 mg Rh were evaporated to dryness on a water bath with concentrated hydrochloric acid, dissolved in 10–15 ml water, treated with an excess of 2 % aqueous (diluted alcoholic) oxime solution, 5 ml Britton–Robinson's buffer solution and warmed on a sand bath for 60 minutes. The volume was completed to 25 ml with the solvent and the absorbance was measured at 440 nm. For the analytical measurements a F.E.K.-colorimeter (made in USSR) was used.

The isomolar solutions were prepared from  $10^{-2}$  mol/l  $\text{RhCl}_3$  and  $10^{-2}$  mol/l chelating agent in 10 ml Britton–Robinson's buffer solution by heating on a sand bath for 60 minutes, cooled and completed to 25 ml.

The *electronic spectra* were taken in Britton–Robinson's buffer solutions using a SPECORD spectrophotometer (Carl Zeiss Jena, Germany). Molar ratio:  $\text{Rh}^{3+}$ :oxime = 1:5.

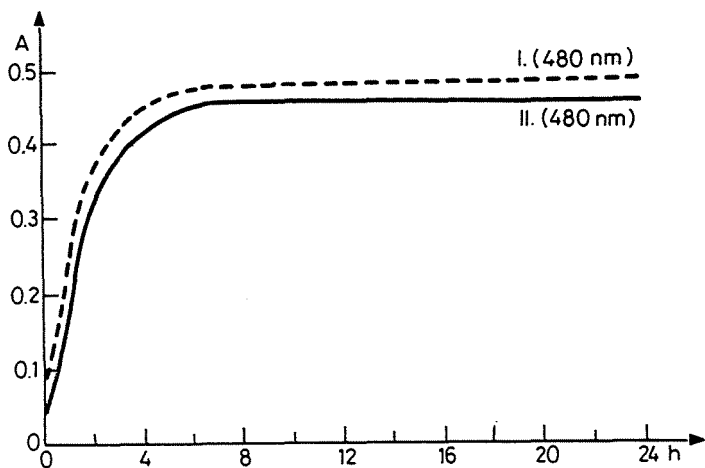


Fig. 11. Stability of the colour intensity in time

I.  $\text{RhCl}_3$ -1,2,3-cyclohexane trione dioxime (1,3)-semicarbazone system ( $\text{Rh}/\text{L}=1:5$ )

II.  $\text{RhCl}_3$ -diacetylmonoxime-thiosemicarbazone system ( $\text{Rh}/\text{L}=1:5$ )

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