

Joanna Maślowska, Waclaw Zakrzewski

CHROMATOGRAPHY OF METAL CHELATE COMPLEXES.

IV. COMPLEXES OF Fe(III), Cr(III) AND Al(III) WITH  
NITROSO-R-SALT

A new method of chromatographic paper was elaborated of separating a mixture of cations: Fe(III), Cr(III) and Al(III) from a medium containing nitroso-R-salt (NRS) as a complexogenic agent.

Nitrosonaphthals are known and often used in chemical analysis reagents which chelate and form complexes with metal ions [1, 2]. Bisodium 1-nitroso-2-hydroxy-napthalene-3,6-bisulphonate, called nitroso-R-salt (NRS) belongs to this group. Thanks to the presence of hydrophile sulphonate groups it is soluble in water and is very active in relation to metal ions contained in aqueous solutions. NRS is a known specific reagent used in colorimetric determination of cobalt [2-6], forming with it a coloured chelate, also stable in acidic media [6, 7]. NRS also forms characteristic chelate complexes with metals such as: Fe(II) and Fe(III) [4, 7-9], Cr(III) [4, 10, 11], Th(IV) [4, 7], Ni(II) [7], VO<sub>2</sub>(II)[12], Cu(II)[4], Zr(IV)[13], Pd(II)[14] and other platinum metals [15-17]. According to Sangal [4], NRS is a reagent particularly suitable for the determination of Pd(II) in the presence of other platinum metals, e.g. Re(III) and Rh(III), since with NRS they form complexes only at higher temperatures. Reactions of NRS with trivalent metals are relatively poorly known. Among three interesting for us ions i.e.

Fe(III), Cr(III) and Al(III) only the system Fe(III)-NRS-H<sub>2</sub>O was the object of studies of some workers [9, 18]. Oka and Miyamoto [18] established in this system the formation of a green very strong complex Fe(NRS)<sub>3</sub> with the stability constant β<sub>3</sub> = 23 (25°), Dean and Lady [19] and Quast [20] used NRS in the determination of iron. Data on Cr(III) complexes is very scarce. Some workers [10, 11] dearly point out the fact that due to the formation of complexes with NRS. Cr(III) interferes in the determination of cobalt and palladium by the method using nitroso-R-salt. The system Al(III)-NRS-H<sub>2</sub>O has not been investigated. Attention has been drawn in this paper to differences in complex forming properties of NRS in relation to Fe(III), Cr(III) and Al(III) ions, to different conditions of complex formation and their different properties, and then these differences were used to distinguish among the mixture of ions investigated by paper chromatography.

### Experimental

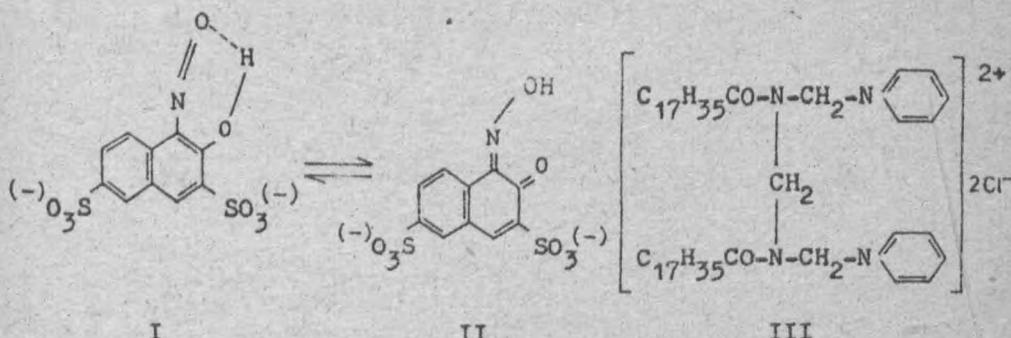
The main equipment reagents and study method were described previously [21-23]. In experiments we also basically used 0,05 M aqueous solution of nitroso-R-salt C<sub>10</sub>H<sub>4</sub>(OH)(SO<sub>3</sub>Na)<sub>2</sub>NO prepared from a reagent pure for analysis (POCh-Gliwice). Chromatographic measurements were made by the method of one-direction ascending paper chromatography on strips (20 x 6 or 20 x 8 cm): fitrak No 389, Whatman No 2 and Whatman No 2 impregnated with hydrophobol IW. Hydrophobol IW (formula III) is a cation active compound as a product of condensation of stearin chloride with sextamethylenetetraamine und piridine. The impregnation of paper was done as follows. An adequate weight portion of hydrophobol was crushed and then ground in a mortar with a small quantity of distilled water at the temperature of 40°C and then diluted with water to the volume of 400 cm<sup>3</sup>. The obtained suspension was forced through a dense cloth and water was added to the volume of 1000 cm<sup>3</sup>. The prepared solution was poured into a glass tub with the dimensions 10 x 4 x 4 cm and after the solution reached the temperature of 20°C strips of paper were

dipped into the solution, and then they were hung to freely dry. The strips covered with a film of hydrophobol were dried at room temperature for 24 hours.

### Results of experiments and discussion

#### Characteristic properties of complexes forming in the systems Me(III)-NRS-H<sub>2</sub>O

It was stated by a method of pH-metric titration that coloured complexes form in the systems Fe(III)-NRS-H<sub>2</sub>O and Cr(III)-NRS-H<sub>2</sub>O. In the first system a red complex is formed at pH = 1.0-2.5 and it turns green at greater pH values. In the second system an orange complex forms only at the solution whole range of pH. Absorption spectra shown in Fig. 1-5 confirm these observations. They gave more evidence for the complexing reactions running also in the system Al(III)-NRS-H<sub>2</sub>O. Absorption spectra of nitroso-R-salt shown in Fig. 1 indicate that this reagent exists in two forms I and II, depending on the medium pH.



Phenol form I which dominates in acidic and neutral mediums is yellow and has the bands  $\lambda = 222, 270$  and  $375$  nm. Quinonoid form II, which dominates in alkaline medium has characteristic green colour and a band  $\lambda = 430$  nm. According to data from Fig. 2-5 spectra of aquocomplexes Fe(III), Cr(III) and Al(III) undergo distinct changes after the addition of NRS.

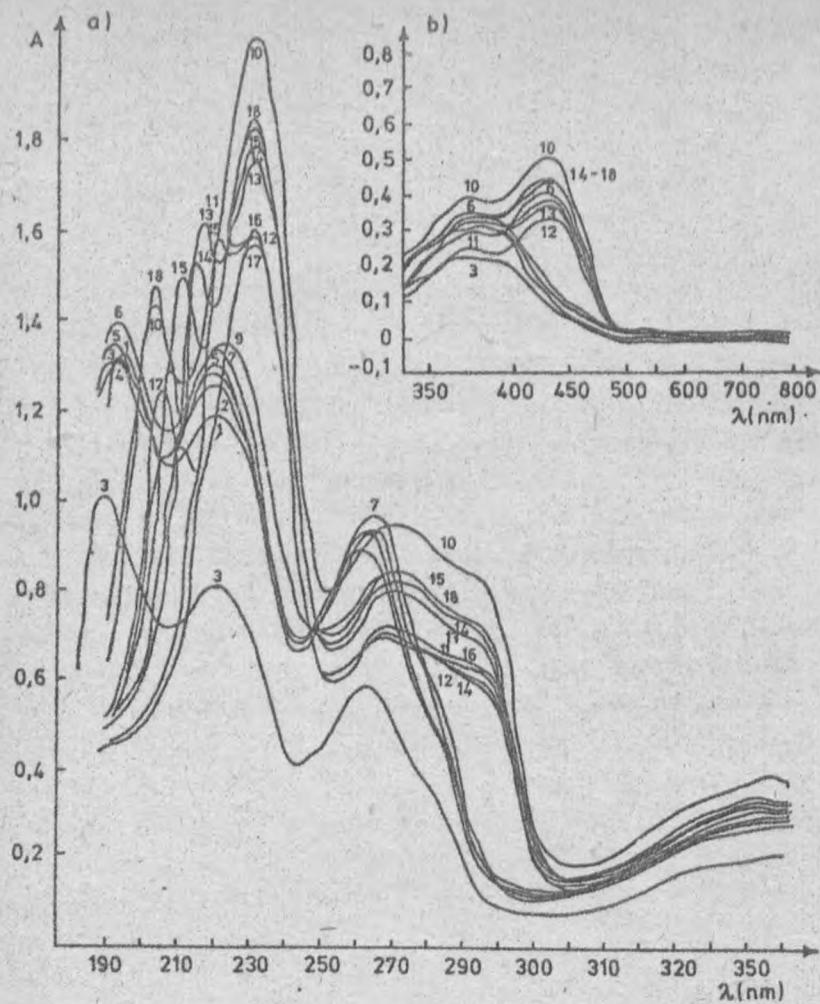


Fig. 1. Absorption spectra of  $1 \times 10^{-3}$  M aqueous solutions of nitroso-R-salts in the UV(a) and visible (b) region. pH of solutions: curve 1 - 0; 2 - 2.0; 3 - 1.5; 4 - 2.0; 5 - 2.5; 6 - 3.0; 7 - 4.0; 8 - 5.0; 9 - 6.0.

Absolutely new absorption bands form in these systems indicating occurring complexing reactions. The formed complexes belong to chelate complexes and can be described by general formula IV or V.

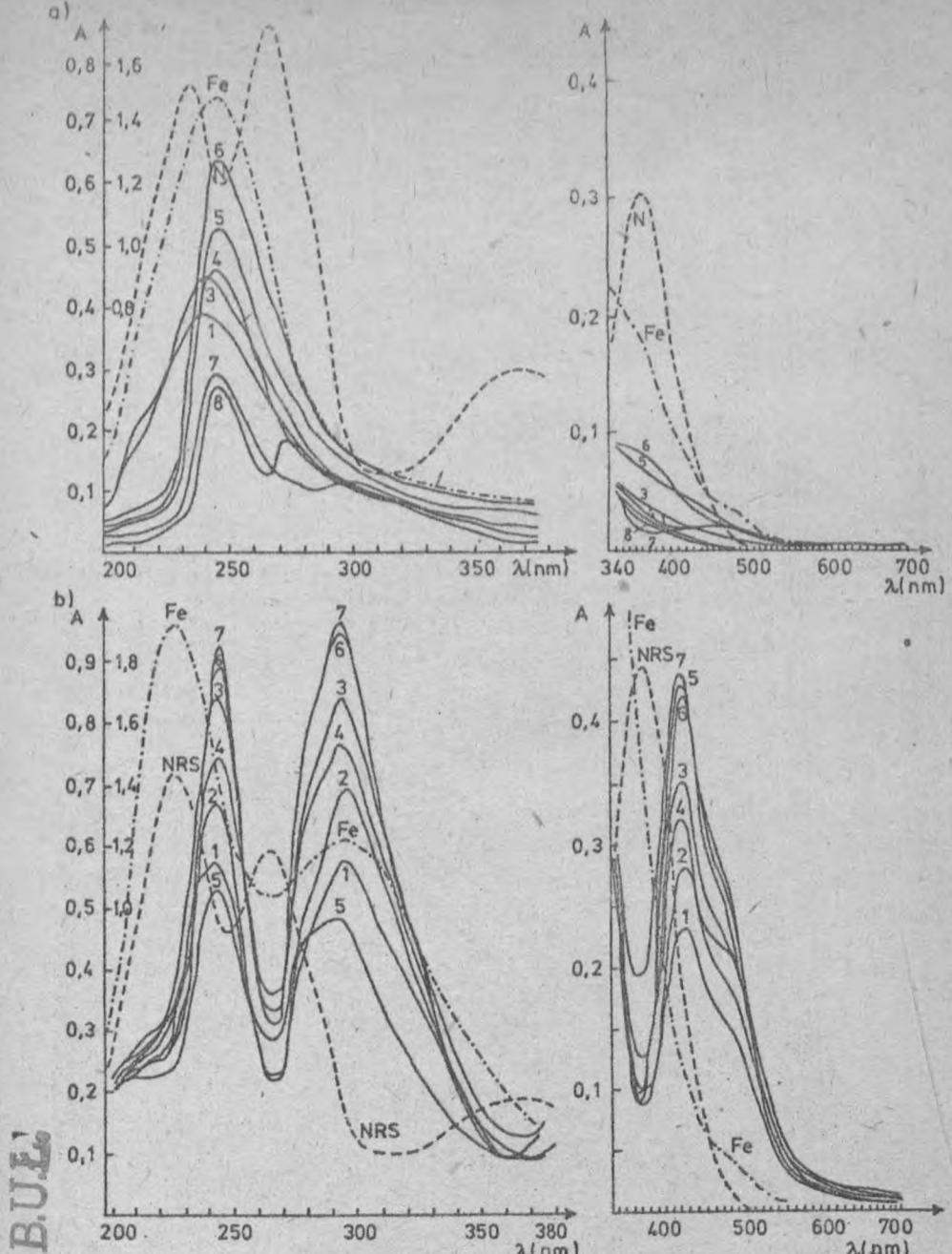


Fig. 2. Effect of nitroso-R-salt concentration on the spectrum of aqueous solution of  $\text{Fe}(\text{ClO}_4)_3$ ; pH = 2.5 (a) and 7.0 (b);  $\text{Fe}^{3+}$  concentration -  $1.0 \times 10^{-5}$  (a) and  $5 \times 10^{-5}$  (b) gion/dm<sup>3</sup>; NRS concentrations; curve 1 -  $5 \times 10^{-5}$ ; 2 -  $6 \times 10^{-5}$ ; 3 -  $7 \times 10^{-5}$ ; 4 -  $8 \times 10^{-5}$ ; 5 -  $9 \times 10^{-5}$ ; 6 -  $1 \times 10^{-4}$ ; 7 -  $2 \times 10^{-4}$ ; 8 -  $3 \times 10^{-4}$ ; d = 1 cm

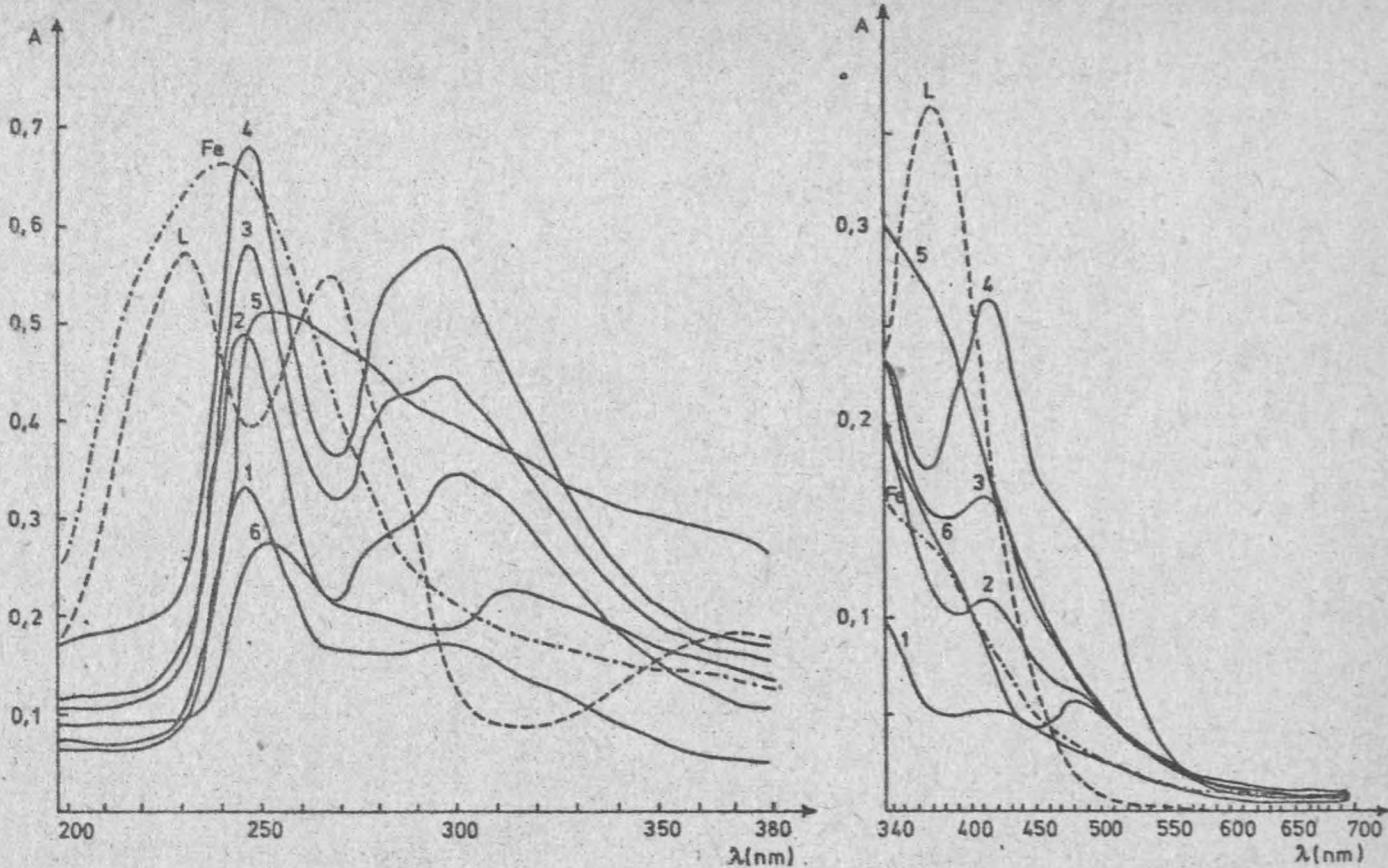


Fig. 3. Effect of pH on the spectrum of  $1 \times 10^{-5}$  M aqueous solution of  $\text{Fe}(\text{ClO}_4)_3$  in the presence of  $1 \times 10^{-4}$  M aqueous solution of nitroso-R-salt. pH: 1 - 2.0; 2 - 4.0; 3 - 6.0; 4 - 7.0; 5 - 8.0; 6 - 9.0;  $d = 1 \text{ cm}$

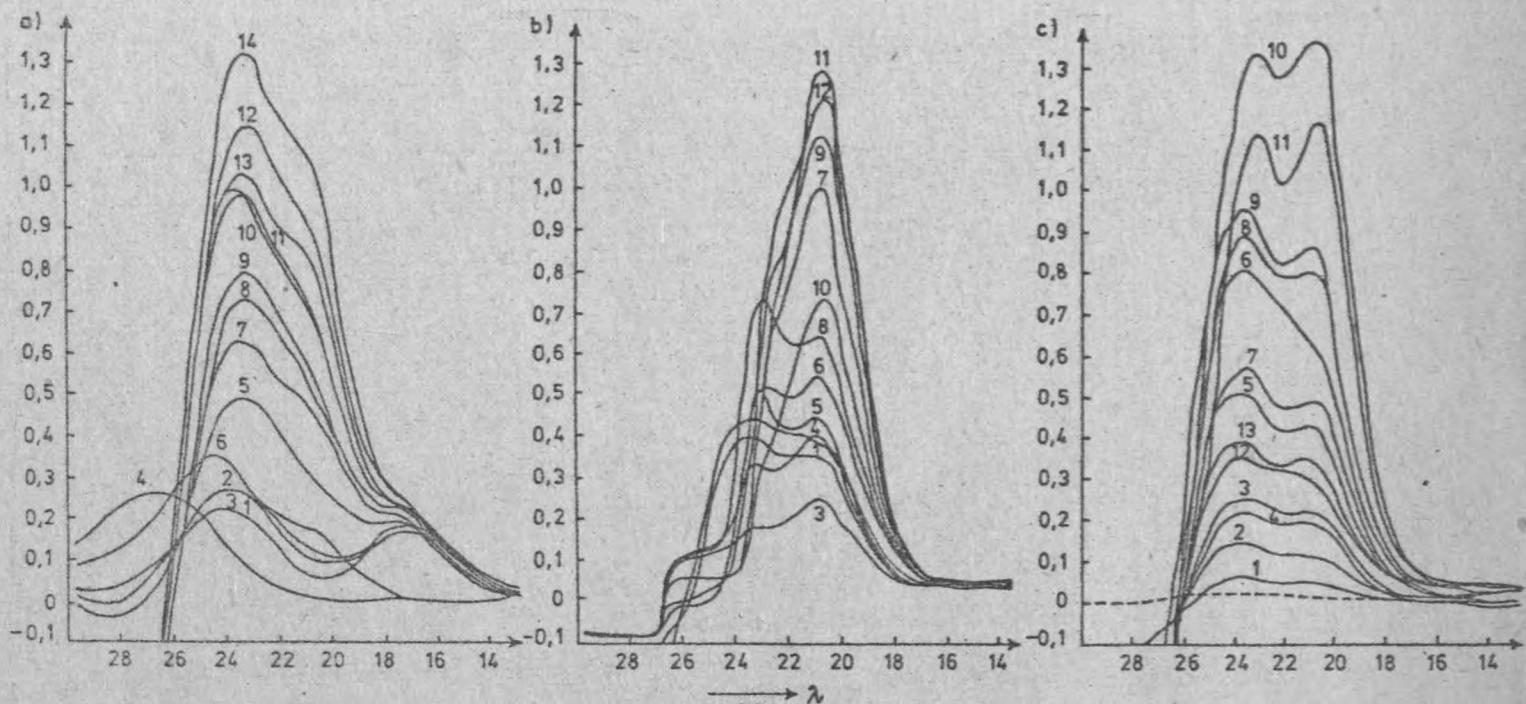


Fig. 4. Absorption spectra in the system  $\text{Cr}(\text{NO}_3)_3$ - NRS- $\text{H}_2\text{O}$   $d = 1 \text{ cm}$ . Samples after boiling and cooling down to room temperature

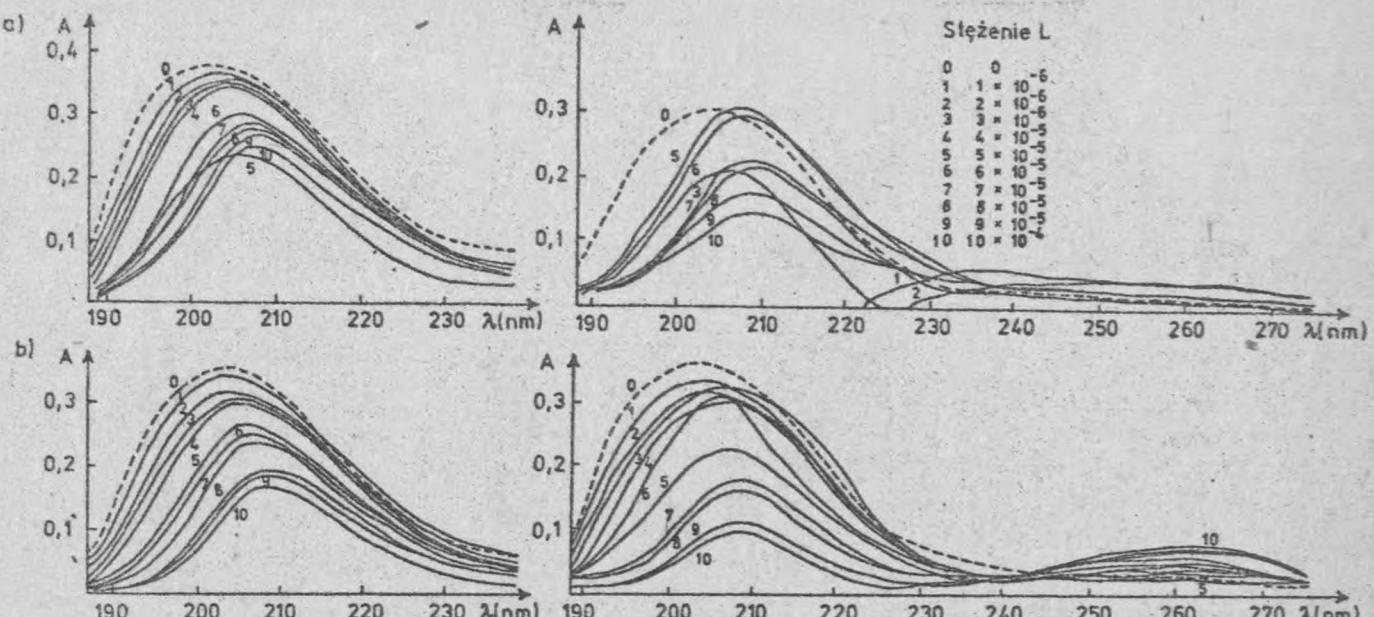
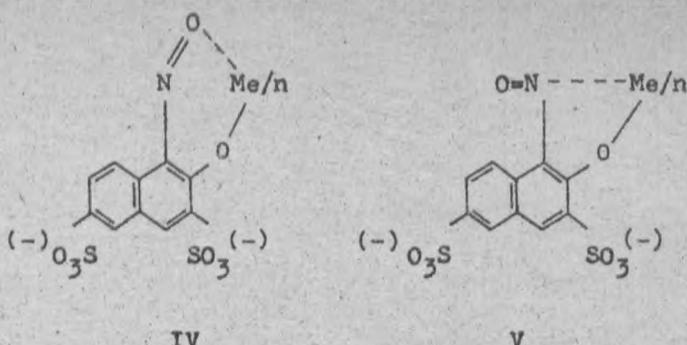


Fig. 5. Absorption spectra in the system  $\text{Al}(\text{NO}_3)_3\text{-NRS-H}_2\text{O}$



Chromatographic separation of a mixture of Fe(III), Cr(III) and Al(III) ions from a medium containing nitroso-R-salt

Calculated and measured volumes of titrated solutions of Al(III), Cr(III) and Fe(III) salts were mixed at the ratio Me: I = 1:2; 1:10 or 1:30 and then in aim to form a Cr(III) complex the prepared solutions were boiled for 3 minutes. During boiling the green iron complex  $\text{Fe}(\text{NRS})_3$  loses its colour since according to Borkowskij and Sołonienko [8] and Tolomaczew and Baszkiński [9], this complex decomposes at the temperature of boiling. In our experiments we established that after some ten hours of storage of such solutions the complex forms again and is stable at room temperature. For these reasons all the prepared and boiled solutions were left for 12 hours to obtain equilibrium state. Solutions of complexes prepared in such a way were applied onto the paper at initial line.

Table 1 and Fig. 6 show data illustrating the varying values of  $R_F$  coefficients as function of the hydrophobol IW concentration in the solution used to impregnate paper strips. From these data it follows that the greatest differences in  $R_F$  values for investigated ions are obtained at the hydrophobol IW concentration of  $2 \text{ g}/\text{dm}^3$ . At such a concentration of hydrophobol IW in the impregnating solution the  $R_F$  values are:  $\text{Fe}^{3+}$  - 0.97;  $\text{Cr}^{3+}$  - 0.84;  $\text{Al}^{3+}$  - 0.22.

Table 1

Values of coefficients  $R_F$  for Me(III) ions  
as function of hydrophobol concentrations in solution used  
to impregnate strips of Whatman No 2 paper; pH = 6

Me(III)	Hydrophobol concentration IW g/cm <sup>3</sup>						
	0	1	2	3	4	5	6
	$R_F$ coefficients						
Fe(III)	1.00	1.00	0.97	0.89	0.87	0.85	0.85
Cr(III)	0.97	0.90	0.84	0.82	0.81	0.79	0.79
Al(III)	0.28	0.26	0.22	0.20	0.20	0.20	0.20

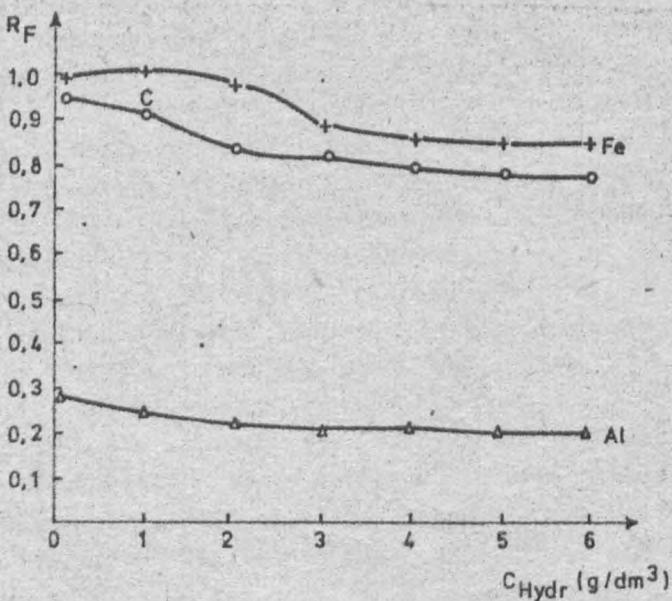


Fig. 6. Variations of the values of coefficients  $R_F$  for Me(III) ions as function of hydrophobol IW concentration in the solution used to impregnate paper strips. Evolution time 2 hours

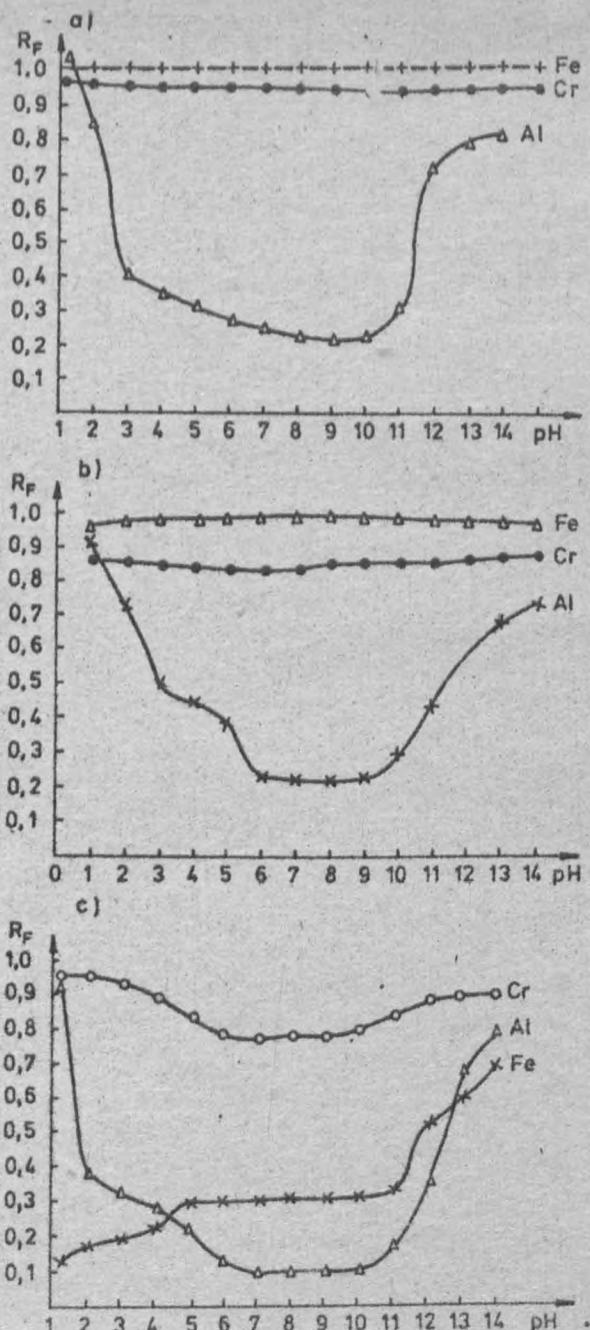


Fig. 7.  $R_F$  values for complexes of Me(III) and nitro-R-salt as function of solution pH: a) Whatman paper No 2; b) paper impregnated with hydrophobol IW (2 g/dm<sup>3</sup>); c) filtrak paper No 389

Fig. 7 shows variations of  $R_F$  values for the investigated complexes as function of solution pH for the three investigated carriers. It follows from the comparison of obtained curves that the greatest differences among the  $R_F$  values are obtained using filtrak paper (Fig. 7c) within the pH range of 6-10. Whatman 2 paper impregnated with hydrophobol IW also presents conditions satisfying the separation of all three cations within the pH range of 3-12 (Fig. 7b). In this case e.g. for pH = 5 the  $R_F$  values are:  $\text{Fe}^{3+}$  - 0.97,  $\text{Cr}^{3+}$  - 0.84 and  $\text{Al}^{3+}$  - 0.35.

Table 2

Values of coefficients  $R_F$  for complexes of Fe (III), Cr (III) and Al (III) determined in the system  $\text{Me}(\text{III})\text{-nitroso-R-salt-H}_2\text{O}$  on various papers

pH	Numeric values $R_F$						Filtrak paper No 389		
	whatman paper No 2			whatman paper No 2 impregnated with hydrophobol IW (2 g/dm <sup>3</sup> )					
	Fe	Cr	Al	Fe	Cr	Al	Fe	Cr	Al
1	1.00	0.97	1	0.95	0.87	0.92	0.14	0.97	0.97
2	1.00	0.97	0.85	0.96	0.86	0.73	0.17	0.97	0.40
3	1.00	0.97	0.40	0.97	0.85	0.50	0.19	0.95	0.32
4	1.00	0.97	0.35	0.97	0.84	0.45	0.21	0.90	0.30
5	1.00	0.96	0.30	0.97	0.84	0.40	0.30	0.85	0.22
6	1.00	0.95	0.28	0.97	0.84	0.22	0.30	0.80	0.14
7	1.00	0.95	0.25	0.97	0.84	0.22	0.30	0.80	0.10
8	1.00	0.95	0.22	0.97	0.85	0.22	0.30	0.80	0.10
9	1.00	0.95	0.23	0.97	0.86	0.22	0.30	0.80	0.10
10	1.00	0.95	0.22	0.96	0.86	0.30	0.30	0.82	0.10
11	1.00	0.95	0.30	0.96	0.86	0.43	0.32	0.82	0.19
12	1.00	0.95	0.74	0.96	0.86	0.45	0.50	0.89	0.40
13	1.00	0.95	0.80	0.96	0.85	0.69	0.60	0.90	0.70
14	1.00	0.95	0.84	0.96	0.86	0.7	0.70	0.90	0.80

Fig. 8, gives some illustrations of obtained chromatograms which show that the above two cases yield full separation and the contours are sharp.

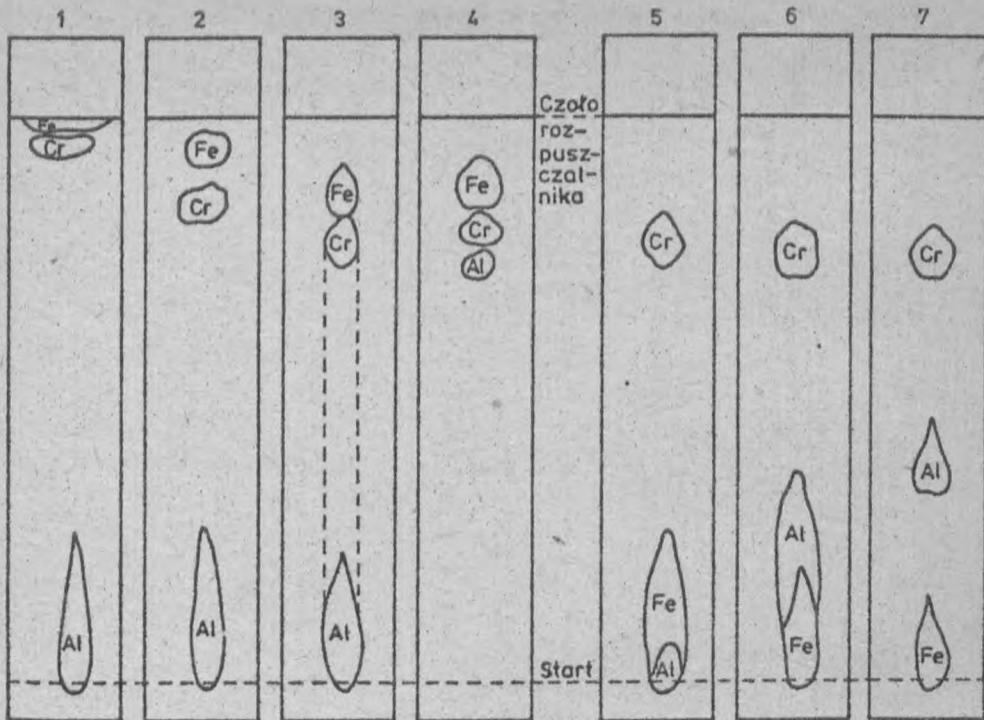


Fig. 8. Examples of chromatograms in the system Me III -nitroso-R-salt-H<sub>2</sub>O i paper W-1; pH = 6; 2-impregnated paper (2 g/dm<sup>3</sup>) pH = 6; 3-impregnated paper (6 g/dm<sup>3</sup>) pH = 6; 4-impregnated paper (2 g/dm<sup>3</sup>); pH = 14; 5-filtrak 389; pH = 6; 6-filtrak 389; pH = 4; 7-filtrak 389; pH = 2.5; way of solvent 15 cm

#### REFERENCES

- [1] Nakamoto K., McCarthy P. J., Spectroscopy and Strukture of Metal Chelate Compounds, New York (1968).
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IV. KOMPLEKSY Fe(III), Cr(III) i Al(III) Z NITROZO-R-SOLĄ

Opracowano nową metodę rozdzielania mieszaniny jonów Fe(III), Cr(III) i Al(III) opartą na chromatografii bibułowej kompleksów tych metali z nitrozo-R-solą. Wykazano, że nitrozo-R-sól tworzy z badanymi kationami kompleksy posiadające wiasne pasma pochłaniania oraz różniące się parametrami chromatograficznymi. Różnice te są na tyle duże, że pozwalają na pełne rozdzielenie mieszaniny jonów w procesie chromatografii bibułowej.

Еания Масловска, Вацлав Закжевски

ХРОМАТОГРАФИЧЕСКИЙ АНАЛИЗ  
КОМПЛЕКСНЫХ ХЕЛАТНЫХ СОЕДИНЕНИЙ МЕТАЛЛОВ.  
IV. КОМПЛЕКСНЫЕ СОЕДИНЕНИЯ Fe(III), Cr(III) и Al(III)  
С НИТРОЗО-Р-СОЛЬЮМ

В работе разработан новый хроматографический метод на бумаге разделения смеси катионов: Fe(III)Cr(III) и Al(III) из среды содержащей нитроzo-R-соль, как комплексующий агент. Установлено, что нитроzo-R-соль составляет комплексные соединения в водном растворе с ионами Me(III). Комплексные соединения имеют собственные полосы спектро поглощения, а также отличаются другими величинами коэффициентов и другими хроматографическими величинами по сравнению с свободными ионами металлов  $Me^{3+}$ . Эти разницы позволяют на полные разделение смеси на бумаге.

B.U.L.

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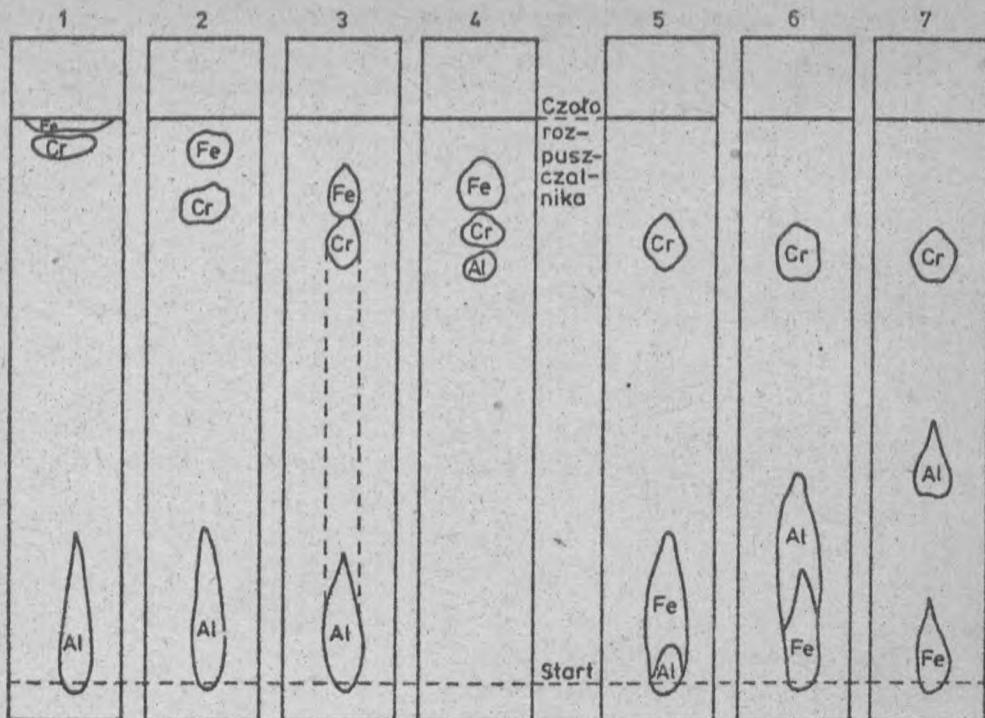


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ХРОМАТОГРАФИЧЕСКИЙ АНАЛИЗ  
КОМПЛЕКСНЫХ ХЕЛАТНЫХ СОЕДИНЕНИЙ МЕТАЛЛОВ.  
IV. КОМПЛЕКСНЫЕ СОЕДИНЕНИЯ Fe(III), Cr(III) и Al(III)  
С НИТРОЗО-Р-СОЛЬЮМ

В работе разработан новый хроматографический метод на бумаге разделения смеси катионов: Fe(III)Cr(III) и Al(III) из среды содержащей нитрозо-Р-соль, как комплексующий агент. Установлено, что нитрозо-Р-соль составляет комплексные соединения в водном растворе с ионами Me(III). Комплексные соединения имеют собственные полосы спектро поглощения, а также отличаются другими величинами коэффициентов и другими хроматографическими величинами по сравнению с свободными ионами металлов  $Me^{3+}$ . Эти разницы позволяют на полные разделение смеси на бумаге.

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