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CHROMATOGRAPHY OF CHELATE METAL COMPLEXES.

V. COMPLEXES OF Fe(III), Cr(III) AND Al(III) WITH VIOLET R\*

A new method of chromatographic paper separation of a mixture of ions Fe(III), Cr(III) and Al(III) has been elaborated with the use of differences of complexogenic properties of violet R in respect of the particular ions.

Organic dyestuffs are often used in chemical analysis as complexometric indicators [1-3]. These substances also have a special meaning in photometric determination of metals which do not have any chromophore properties. The reactions of dyes with ions of metals with chromophore properties are often less specific. According to some authors [4], the formation of a dye complex with metal cation is often analogous to the formation of an additional auxochrome in the conpling chain. Sano [5] investigated the problem of the specific influence of particular metal ions on the shift of the dye absorption band. In many cases the problem of the absorption band shift turned out to be complex since often it is not the free metal ions that react but their hydrolized forms [6]. Azo dyes eg. derivatives of salicyl acid do not change their colour during the formation of complexes with aluminium ions.

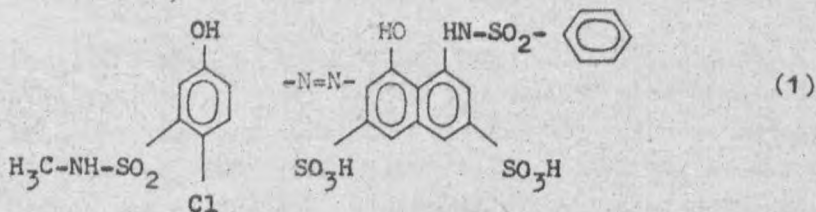
Searching for further [11] conditions of chromatographic separation of a mixture of ions Fe(III), Cr(III) and Al(III) we looked closer at acid azo dyes of the o,o'-dihydroxyazo

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\* The work has been carried out within the research Problem MR-I-14.

system. Eriochromic black T also belongs to this group of dyes and is used as an indicator in complexometric methods [7] and in spectrophotometric determination of magnesium(II) [8, 9]. Wawrzyniak [10] elaborated a method of formation of stable complexes on fibres of such dyes with Co(II), Cu(II), Ni(II) and Cr(III). These complexes are formed only at increased temperature.

The o,o'-dihydroxyazosystem is not characteristic for Al(III), but for Fe(III) but these complexes are not well known. One could expect a big difference in the complexation of three investigated metal ions with a o,o'-dihydroxyazo-dye and hence the suitability of such dyes for chromatographic separation of ions: Fe(III), Al(III) and Cr(III). A dye called violet R, with formula (1), was chosen for investigations.



This dye is obtained by diazotization of a 2-aminephenole-4-chloro-5-sulphonethenylamide and coupling with the 1-N-phenylsulphonyloamine-8-hydroxynaphthalene-3,6-disulphonic acid. This dye was obtained in the Institute of Fibre Physics at the Polytechnical University of Łódź.

In this paper we emphasized differences in the complexogenic properties of violet R in relation to Fe(III), Cr(III) and Al(III) ions, various conditions of the formation of complexes and their different properties and then we took advantage of these differences in the paper chromatographic separation of the mixture of ions.

### Experimental

The basic instruments, reagents and method of investigations has been described earlier [11]. For pH-metric and spec-

trophotometric investigations we also used solutions of sulphates of aluminium, iron and chromium with the Me(III) concentration =  $1 \times 10^{-4}$  mole.dm<sup>-3</sup> and the ratio Me:L = 1:1. For chromatographic investigations we used solutions of the concentration  $1 \times 10^{-2}$  mole.dm<sup>-3</sup> Me(III) and the ratio Me(III):L = 1:1. During initial investigations we used solvents composed of water and methanol or ethanol and of water and acetone as well as pure water. Aqueous solution of NaCl or aqueous solution of NH<sub>4</sub>OH are often used as developing systems in paper chromatography for the separation of dyes used for foodstuffs and cosmetics [12]. Whatman nr. 2 and Filtrak 390 papers were used as carriers. Sramek [13] successfully used Filtrak paper in the separation of direct dyes. In former paper [14] we also obtained successful separation results using Filtrak 389 paper.

### Results and discussion

#### Characteristic features of complexes formed in the systems:

##### Me(III)-Violet R-H<sub>2</sub>O

Using the method of pH-metric titration we stated that coloured complexes are formed in the systems: Fe(III)-Violet R-H<sub>2</sub>O and Al(III)-Violet R-H<sub>2</sub>O. In the first system within the pH range of 1,0-2,0 a red-violet complex is formed and at higher pH values a violet-grey complex is formed. In the second system within the pH range of 3,5-7 a blue-violet complex is formed and at higher pH values a blue complex is formed. Table 1 gives colours of the solution of the dye itself and of formed complexes depending on the solution pH. The solution of the dye itself as well as the solution of the dye in presence of Cr(III) act in the same way. It means that only Cr(III) does not form complexes with violet R at room temperature. These observations are confirmed by recorded absorption spectra shown in Fig. 1 and characteristic bands given in Table 2. From these bands it follows that Fe(III) complexes have two bands in the visible range ( $\lambda_{\text{max}} = 480$  and 625 nm), and Al(III) complexes one band at 540 nm. The spectrum of the Cr(III) system has the same position as the spectrum of Violet R. The stated shifts of

Table 1

The influence of solution pH on the colour of violet R and of its complexes with metals. Concentration of Me(III) =  $1 \times 10^{-4}$  M/dm<sup>3</sup>; Concentration of dye =  $1 \times 10^{-4}$  M/dm<sup>3</sup>; Me(III) : L = 1:1

Solution pH	Colour of solution			
	violet R	violet R + Fe(III)	violet R + Cr(III)	violet R + Al(III)
1-2	red	red-violet	red	red
2-3,5	pink	violet-grey	pink	pink
3-4	pink	"	"	blue-violet
5-6	blue	"	blue	"
7-8	"	"	blue + green deposit	blue
8-9	"	"	"	"
9-10	"	"	"	"

Table 2

Specification of  $\lambda_{\max}$  values and of molar coefficient of absorption E for solutions in systems: Me(III)-violet R-H<sub>2</sub>O. Dye concentration =  $1 \times 10^{-4}$  M/dm<sup>3</sup>; Me(III) concentration =  $1 \times 10^{-4}$  M/dm<sup>3</sup>; pH = 3,5; 1 - 1 cm

System	Visible range		UV range	
	$\lambda_{\max}$ . nm	E (cm <sup>2</sup> · mole <sup>-1</sup> )	$\lambda_{\max}$ . nm	E (cm <sup>2</sup> · mole <sup>-1</sup> )
Violet R	520	$7.8 \times 10^3$	230	$8.8 \times 10^3$
			240	$8.4 \times 10^3$
			315	$5.0 \times 10^3$
Violet R-Cr(III)	520	$7.7 \times 10^3$	230	$9.6 \times 10^3$
			240	$9.2 \times 10^3$
			315	$5.2 \times 10^3$
Violet R-Al(III)	540	$7.8 \times 10^3$	210	$12.8 \times 10^3$
			240	$9.2 \times 10^3$
			315	$4.8 \times 10^3$
Violet R-Fe(III)	480	$5.2 \times 10^3$	225	$12.2 \times 10^3$
	625	$1.4 \times 10^3$	240	$12.6 \times 10^3$
			320	$5.6 \times 10^3$



- 1 - violet-R  
 2 - Fe(III) + violet-R  
 3 - Al(III) + violet-R  
 4 - Cr(III) + violet-R

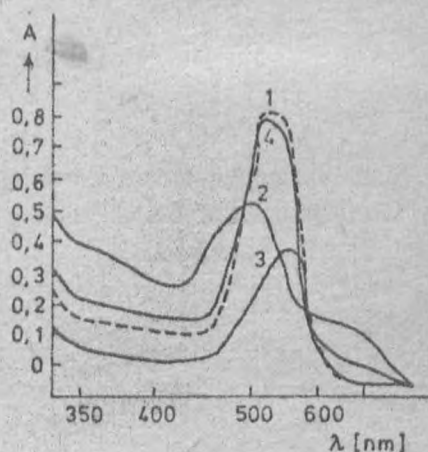
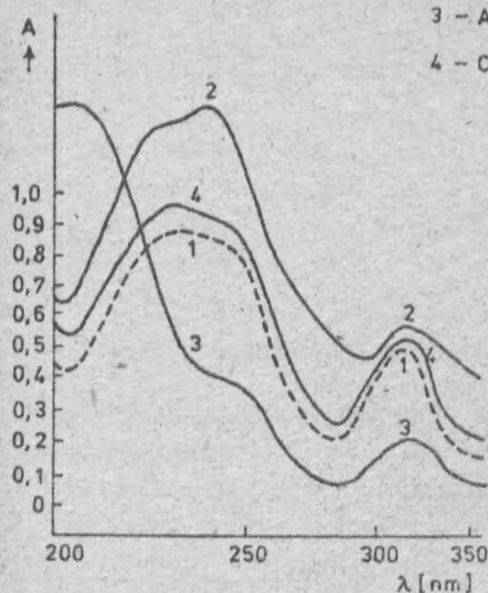


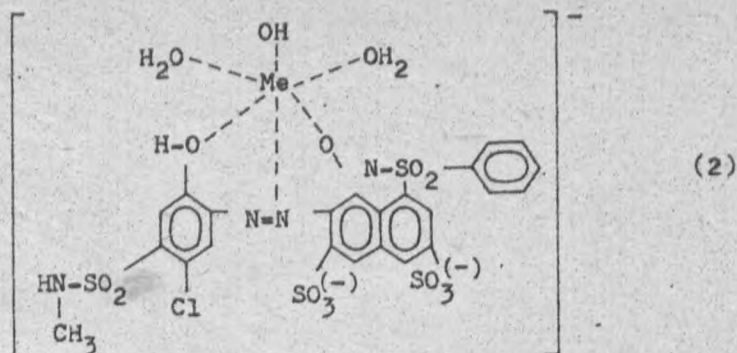
Fig. 1. Absorption spectra of solutions in the system  $\text{Me(III)} - \text{violet R} - \text{H}_2\text{O}$ . Concentration  $[\text{Me}^{3+}] = [\text{violet R}] = 1 \times 10^{-4} \text{ mole} \cdot \text{dm}^{-3}$ . Curves: 1 - violet R; 2 - Fe(III) + violet R; 3 - Al(III) + violet R; 4 - Cr(III) + violet R

absorption bands both in the visible range and in the UV range in the case of Fe(III) and Al(III) as well as the lack of these shifts in the case of Cr(III) allow to presume that Fe(III) and Al(III) form complexes with Violet R and Cr(III) does not form complexes with this reagent in these conditions. Complex reactions of Fe(III) and Al(III) with violet R can be represented by the following equation:



The structure of complexes  $[(\text{MeOH})(\text{HR})]^-$  formed under such

conditions with the composition  $\text{Me} : \text{L} = 1:1$  can be shown by structure 2.



Chromatographic separation of a mixture of ions  $\text{Fe(III)}$ ,  $\text{Cr(III)}$  and  $\text{Al(III)}$  from an environment containing violet R

In initial experiments we used mixed solvents composed of water and methanol or ethanol and of water and acetone obtaining chromatograms with superposed zones of all the three ions. Much better effects are obtained using as a developing system water with

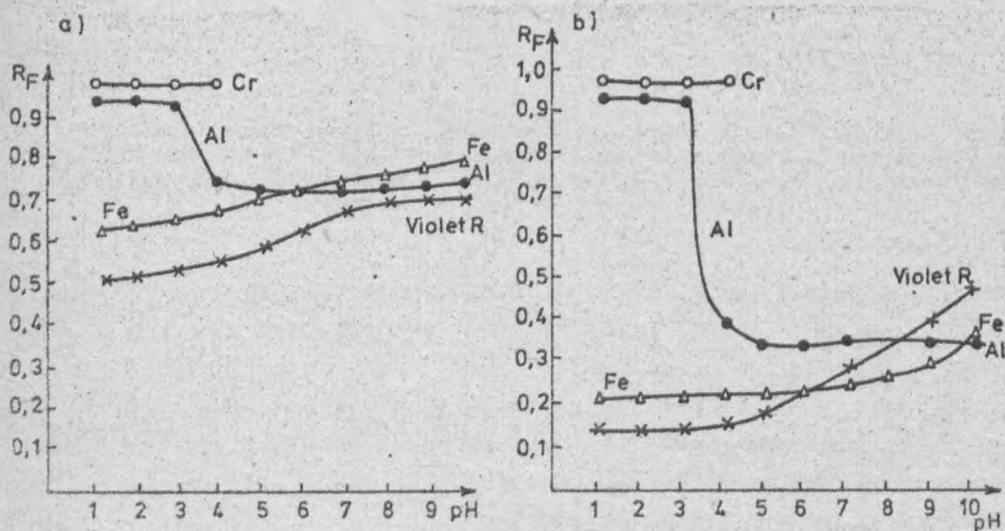


Fig. 2. Plots of values of coefficients  $R_F$  for  $\text{Me(III)}$  complexes with violet R as function of solution pH. Developing system:  $\text{H}_2\text{O} + \text{HClO}_4$  or  $\text{NaOH}$ ; Paper: a - Whatman no 2; b - Filtrak no 390; Time of chromatogram development 75 min

a predetermined pH adjusted with an addition of  $\text{HClO}_4$  or  $\text{NaOH}$ . Comparing results shown in Fig. 2 can notice that when using Filtrak 390 paper the coefficients  $R_F$  for complexes of  $\text{Fe(III)}$  (within the pH range of 4-10) have considerably lower values than when using Whatman paper no 2. Besides the zones of ions obtained on this paper have more regular shapes and sharper outlines. Hence it was acknowledged that Filtrak paper no 390 gives better effects of variations of the spots. Data from Fig. 3 show that in the process of one-stage developing, using water as the solvent, one can separate Fe from  $\text{Cr} + \text{Al}$  at pH 2-3, and Cr from  $\text{Fe} + \text{Al}$  at  $\text{pH} = 4$ . The experiments allowed to assume that using a two-stage process of chromatogram development it would be possible to separate all three ions. Basing on the facts that  $\text{Al(III)}$  forms a complex with violet R at  $\text{pH} = 3, 5$  and  $\text{Fe(III)}$  already at  $\text{pH} = 1$ , and  $\text{Cr(III)}$  at room temperature practically does not form a complex with this dye and that complexes of violet R with  $\text{Al(III)}$  and  $\text{Fe(III)}$  have similar chromatographic parameters (Fig. 3) we thought that the

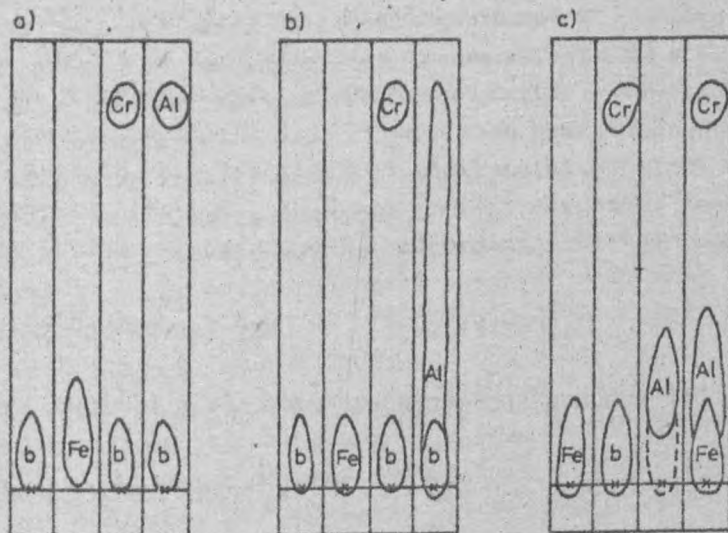
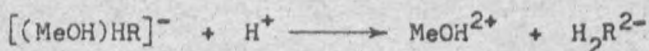


Fig. 3. Chromatograms of a mixture of ions  $\text{Fe(III)}$ ,  $\text{Cr(III)}$  and  $\text{Al(III)}$  in the presence of violet R obtained in one-stage developing system. Filtrak paper no 390, other conditions as per Fig. 2. a)  $\text{pH} = 4$ ; b)  $\text{pH} = 3$ ; c)  $\text{pH} = 2$

use of a solvent of pH smaller than 3,5 in the second stage of developing should cause the freeing of Al(III) from the complex according to the equation:



and enhance its migration in relation to the complex bound iron. Experiments fully confirmed this assumption. Samples of solution containing salts of investigated metals and violet R, with pH = 4 were placed on paper and undergo to development using solvent of pH = 4. During initial chromatography well visible zones of the Al(III) complex and of the Fe(III) complex were slightly shifted apart and the invisible Cr(III) zone was separated from them. The process of initial developing was stopped after 20 minutes and after drying the chromatogram the developing was renewed in the solvent with pH = 2 or 3. When the front of the second solvent crossed the starting line we observed an accelerated migration of the further part of aluminium zone. The change of the solvent had no distinct effect on the migration of zones occupied by iron(III) and chromium(III). After ending the second stage of developing the Al zone in the solvent with pH = 3 was coloured and in the solvent with pH = 2 not coloured and needed make evident (by aluminon). The zone of Cr in both cases required make evident (by EDTA). In both cases the zone of Fe was coloured. The shape of the Fe zone remained conical during the second developing while the shape of the Al zone changed from conical to round. After 15 minutes of initial developing (pH = 4) and after 60 minutes of renewed developing (pH = 2) the coefficients  $R_F$  were as follows: Cr(III) = 0,98; Al(III) = 0,65 and Fe(III) = 0,22. Changing the time of developing in the first and second stage one can change the position of the Al zone in relation to zones of Fe and Cr. Fig. 4 shows some chromatograms obtained in this way, which indicate complete separation of the investigated mixture of cations.

The elaborated method is simple, fast, convenient, and yield very good separations.



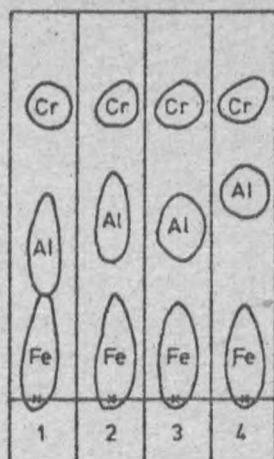


Fig. 4. Chromatograms of a mixture of trivalent ions obtained from a medium containing violet R. Filtrak no 390; Developing system:  $H_2O + HClO_4$ ; Time of initial developing: 1-20; 2-15; 3-25; 4-18 min. Total time of developing 75 min

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#### CHROMATOGRAFIA KOMPLEKSÓW CHELATOWYCH METALI. V. KOMPLEKSY Fe(III), Cr(III) I Al(III) Z FIOLETEM R

Fiolet R przedstawiciel barwników azowych o charakterze kwasowym, posiadający układ O,O'-dwyhydroksyazowy wykorzystano z pomyślnymi wynikami jako czynnik kompleksujący do chromatograficznego rozdzielania na bibule trudnej do rozdzielania innymi metodami mieszaniny kationów trójwartościowych:  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$  i  $\text{Al}^{3+}$ . Stwierdzono, że barwnik ten nie kompleksuje na zimno z Cr(III), a kompleksuje z Fe(III) i Al(III) dając barwne kompleksy o własnych pasmach absorpcyjnych.

Do mieszaniny trzech badanych kationów dodaje się wodny roztwór fioletu R w takiej ilości, aby stosunek każdego jonu Me(III) do barwnika nie był niższy niż 1:1. Chromatografię prowadzi się na paskach bibuły Filtrak 390, stosując w ciągu 15 min. rozwijanie wstępne z  $\text{H}_2\text{O} + \text{HClO}_4$  (pH = 4), a po wysuszeniu paska ponowne rozwijanie w ciągu 60 min. z  $\text{H}_2\text{O} + \text{HClO}_4$  o pH = 2. Otrzymuje się bardzo wyraźne i pełne rozdzielanie. Współczynniki  $R_F$ : Cr(III) - 0,98, Al(III) - 0,65 i Fe(III) - 0,22.

Занна Масловска, Вацлав Закжевски

ХРОМАТОГРАФИЯ ХЕЛАТНЫХ КОМПЛЕКСОВ МЕТАЛЛОВ.  
V. КОМПЛЕКСЫ Fe(III), Cr(III) И Al(III) С ФИОЛЕТОМ R

Исследованы реакции комплексообразования и свойства комплексов Fe(III), Cr(III) и Al(III) в водных растворах фиолета R. Разработан новый хроматографический метод разделения смеси ионов Fe(III), Cr(III) и Al(III). Получены следующие значения  $R_F$ : Cr(III) - 0,98; Al(III) - 0,65 и Fe(III) - 0,22.