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SILICAS WITH IMMOBILIZED XYLENOL ORANGE AND CALCEIN: PREPARATION, COMPLEXING PROPERTIES AND ANALYTICAL USE

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OUTLINE

- Features of silica-organics hybrid materials and preparation routes;
- change of properties of immobilized organic reagent: affecting factors;
- preparation of hybrid materials wih immobilized xylenol orange and calcein;
- complexation equilibria and effects of energetic heterogeneity;
- materials wih immobilized xylenol orange and calcein in test-analysis.

Silica-organics hybrid materials

Hybrid is not the sum of silica and organic modifier!

Properties

- high surface area, regulated capacity, possibility to set up the affinity for target species
- rather favorable kinetic characteristics
- powder, monolith, film, fibre

Preparation routes

- silanization of silica surface
- post-silanization chemical modification
- sol-gel synthesis
- non-covalent immobilization

Some target applications

- sorption
- analysis
- catalysis
- sensors

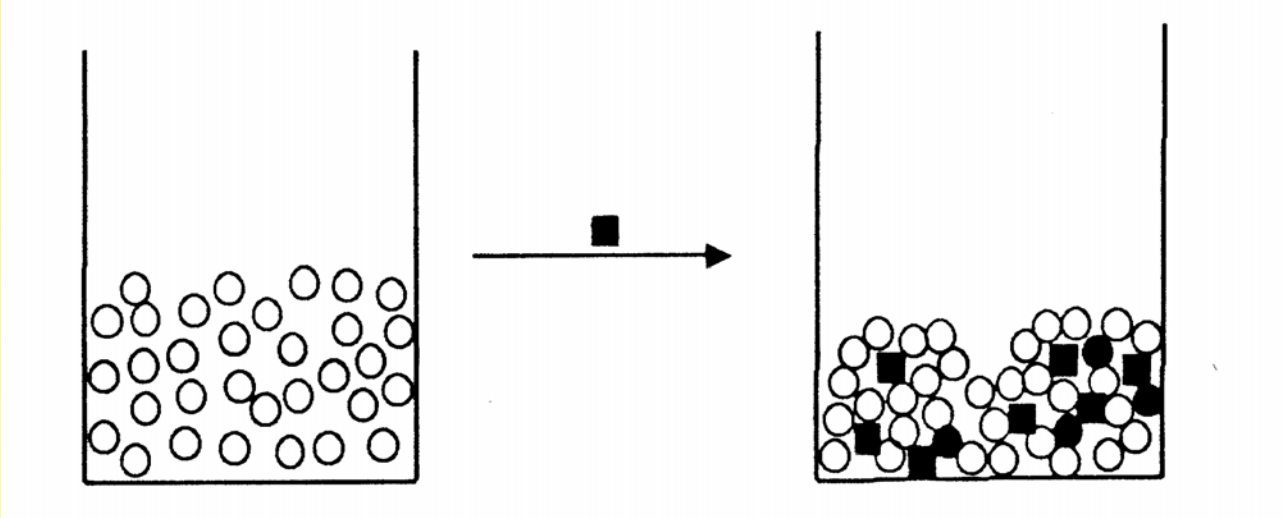
Non-covalent
non-covalent immobilization

Sol-gel technology

Grafting on silica surface

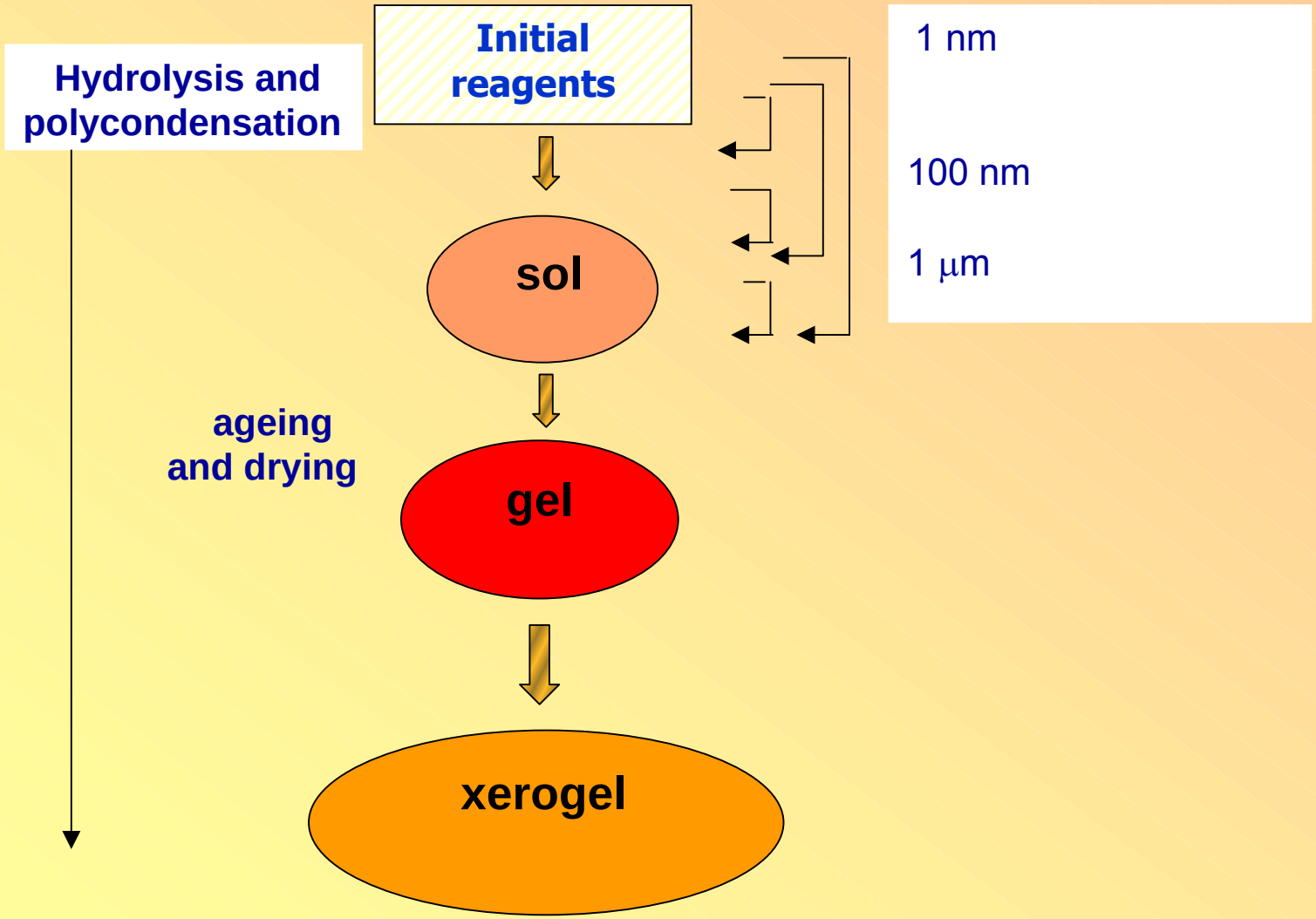
Sol-gel synthesis:
controlled hydrolysis, condensation

Non-covalent immobilization



Sol **Reagent** **Gel**

Main steps of sol-gel process

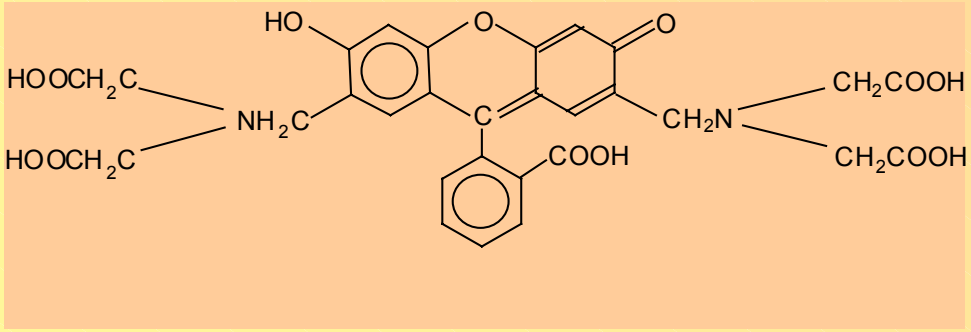


How immobilization of organic reagents affects their affinity to “ligands”?

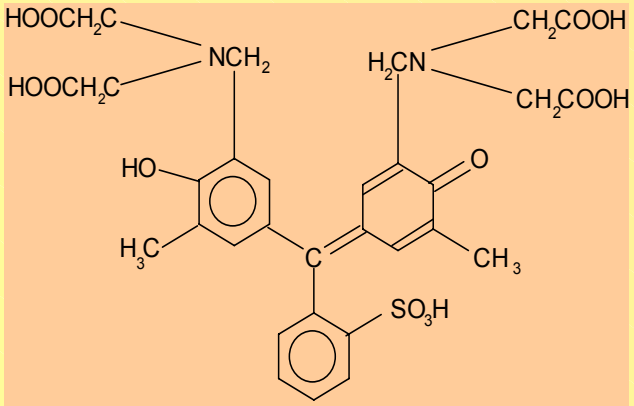
Factors: morphology, surface topography, micro-environment of fixed species, energetic heterogeneity and others

Possible effects: energetic heterogeneity of reagents, cooperativity effects, uncommon composition or/and stability of immobilized complexes, …

Immobilization of complexing dyes



$pK_a = 2.1; 2.9; 4.1; 5.4; 10.1; 12.0$



$pK_a = 2.1; 2.2; 3.6; 7.3; 9.7; 12.6$

Procedure

– 5.0 ml TEOS, 1.5–5.0 ml 0.2-2 mM dye ethanol solution, ethanol (total volume 12 ml),

– catalyst $(NH_4)_2[SiF_6]$,

– formation of gel (3–4 h),

– drying: 10 min, power of microvawe radiation 850 W,

– fraction 250-500 mcm.

Y.Kholin, S. Korneev, I. Khristenko, F. Pissetti, Y. Gushikem, *Methods and Objects of Chem. Anal., 2008, V. 3, No 1.*

Properties of hybrid materials

Specific concentrations up to 45-90 μmol g^{-1}

Surface area

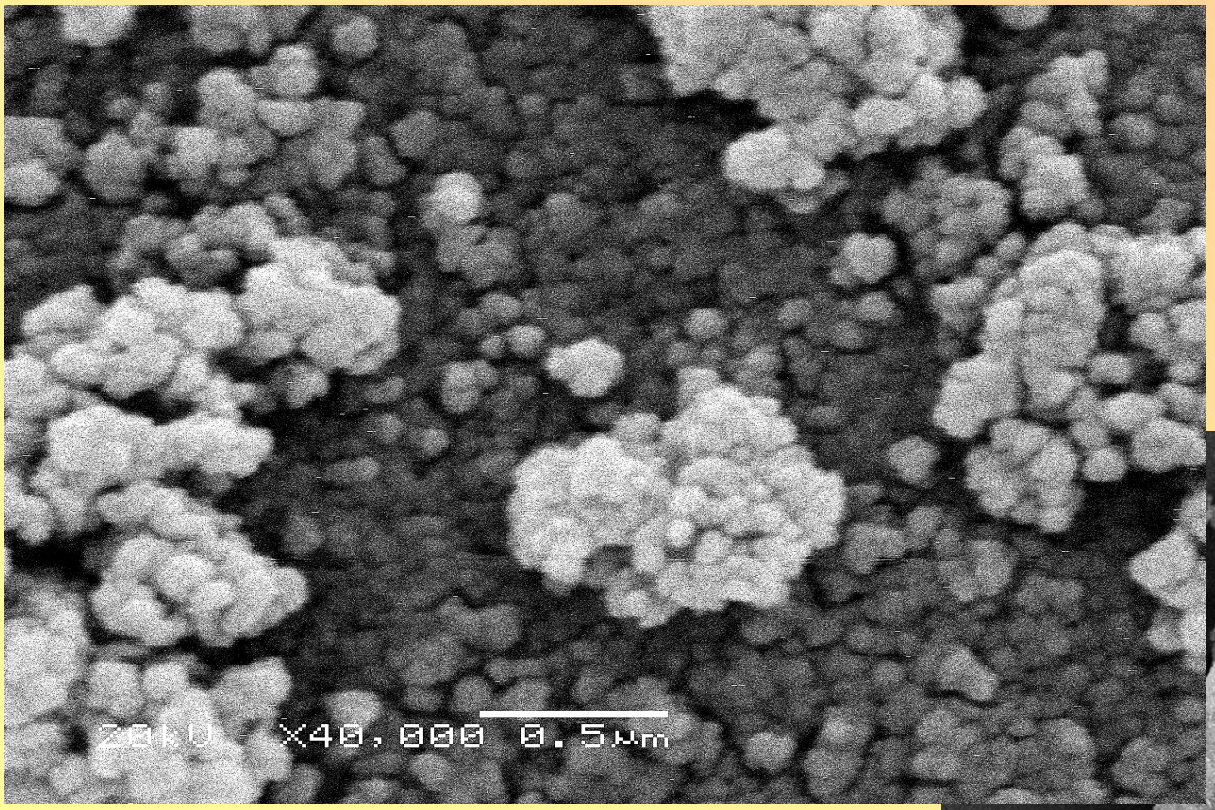
700 m^2 g^{-1}

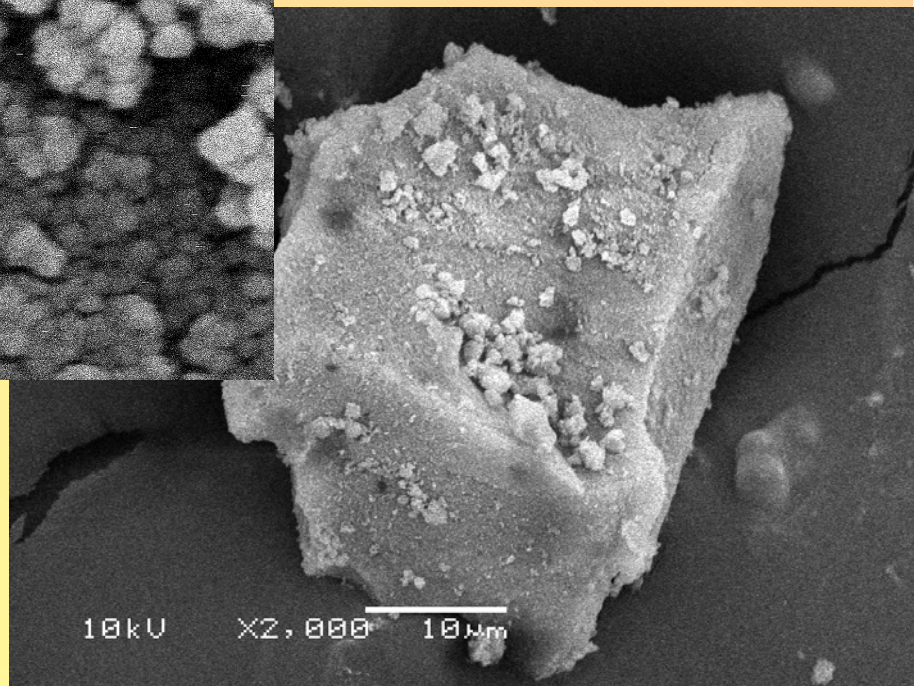
Leaching

of dyes 0-3%

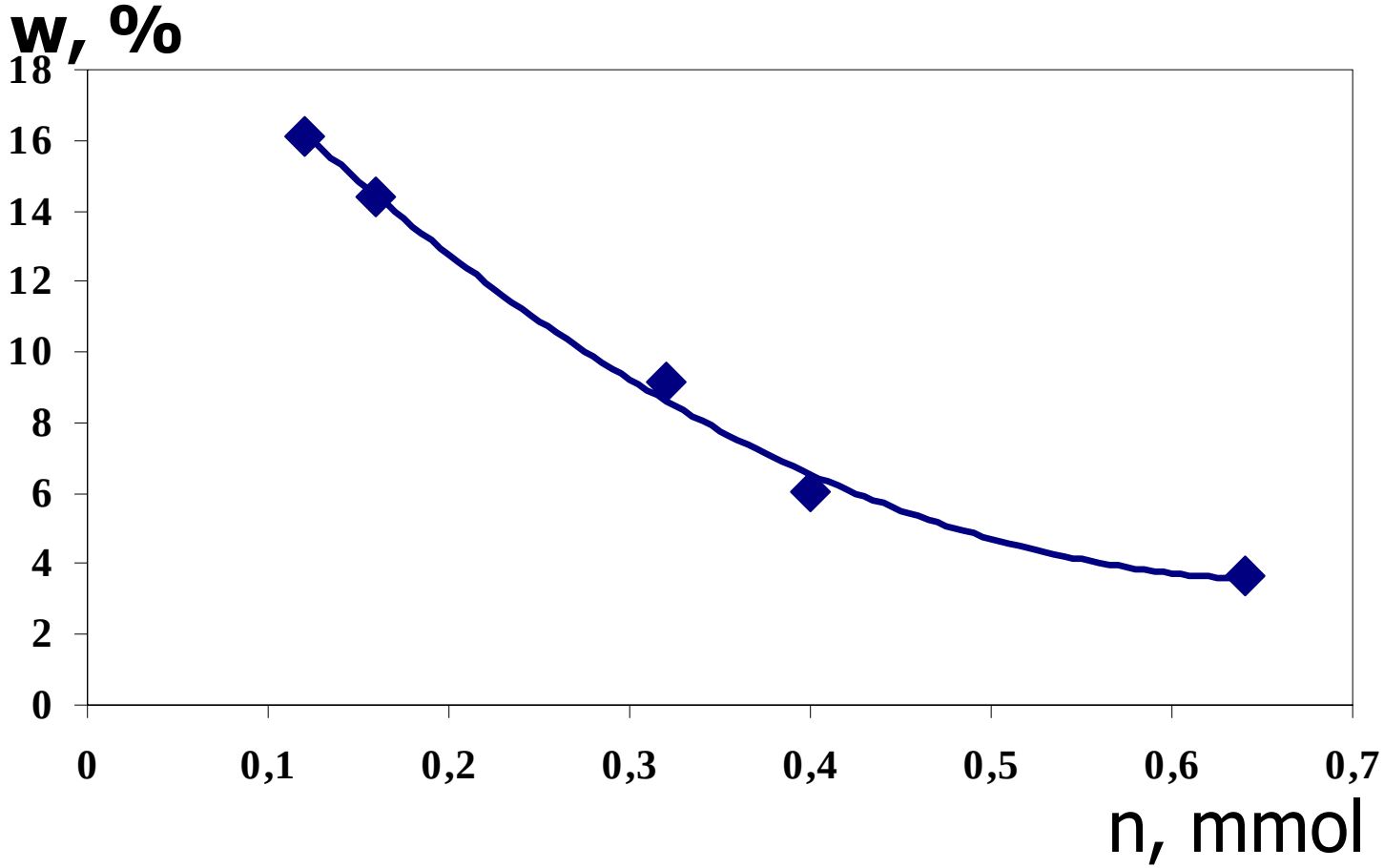
Attainment of sorption equilibrium: up to 15 min

Xerogel with immobilized xylenol orange



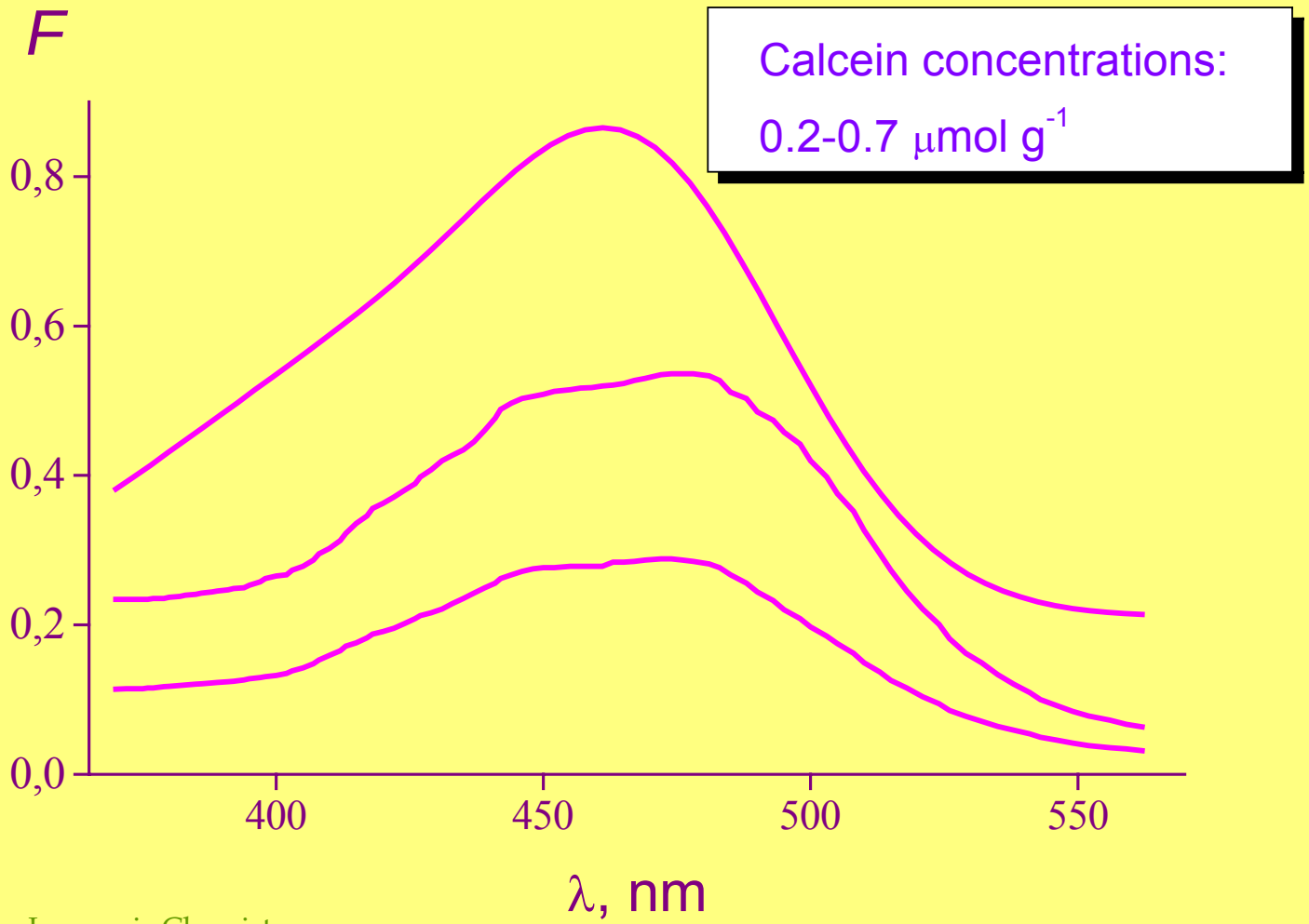


Dependence of xylenol orange leaching (w, %) on the quantity of catalyst $(NH_4)_2[SiF_6]$ (n, mmol).



Absorption spectra of immobilized calcein

Im aqueous solution with pH 3.2: maxima at 454 and 474 nm

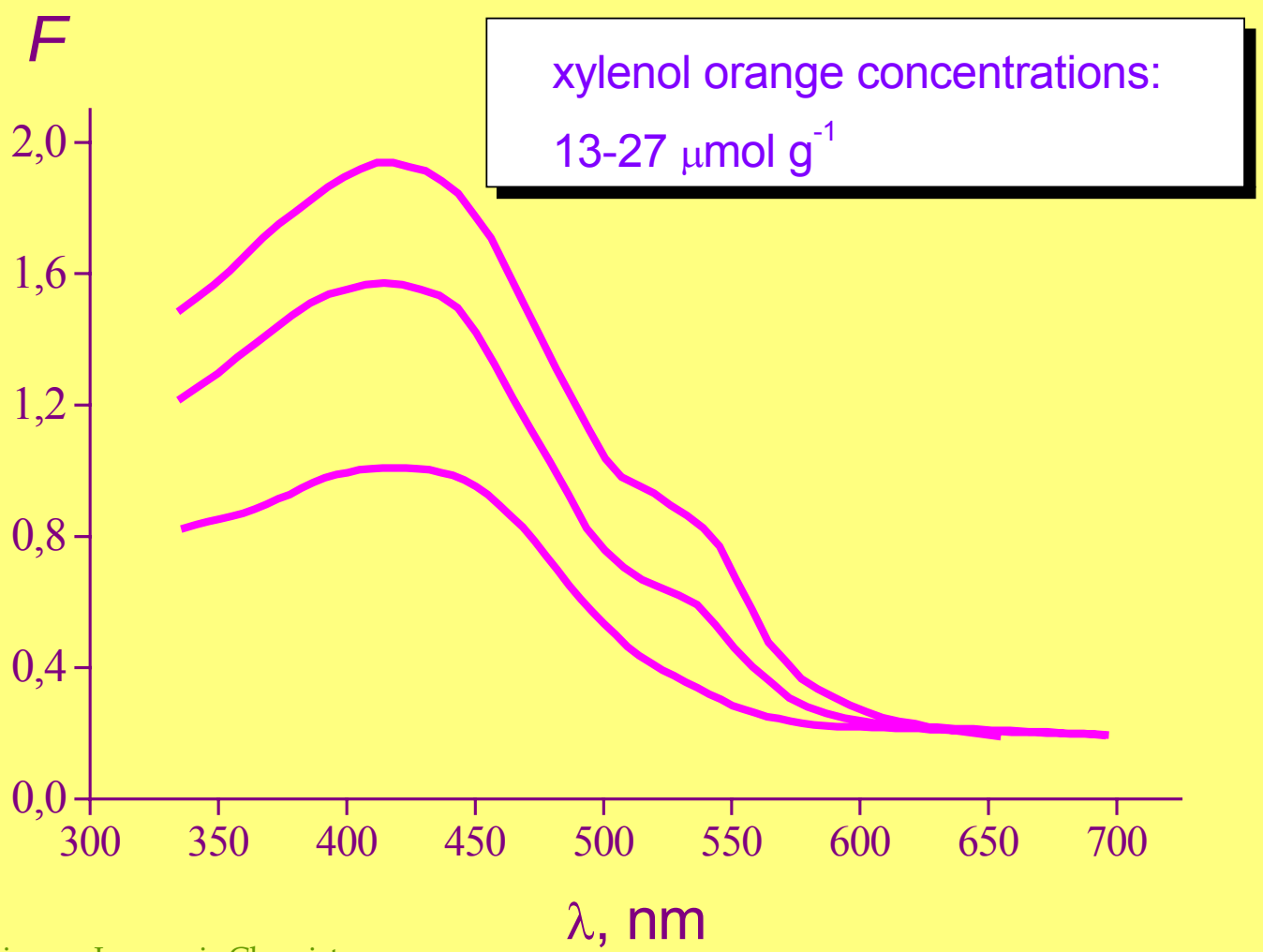


Absorption spectra of immobilized xylenol orange

Aqueous solution

pH 4.5-6.5:
H_3L^{3-} и H_4L^{2}
432-435 nm

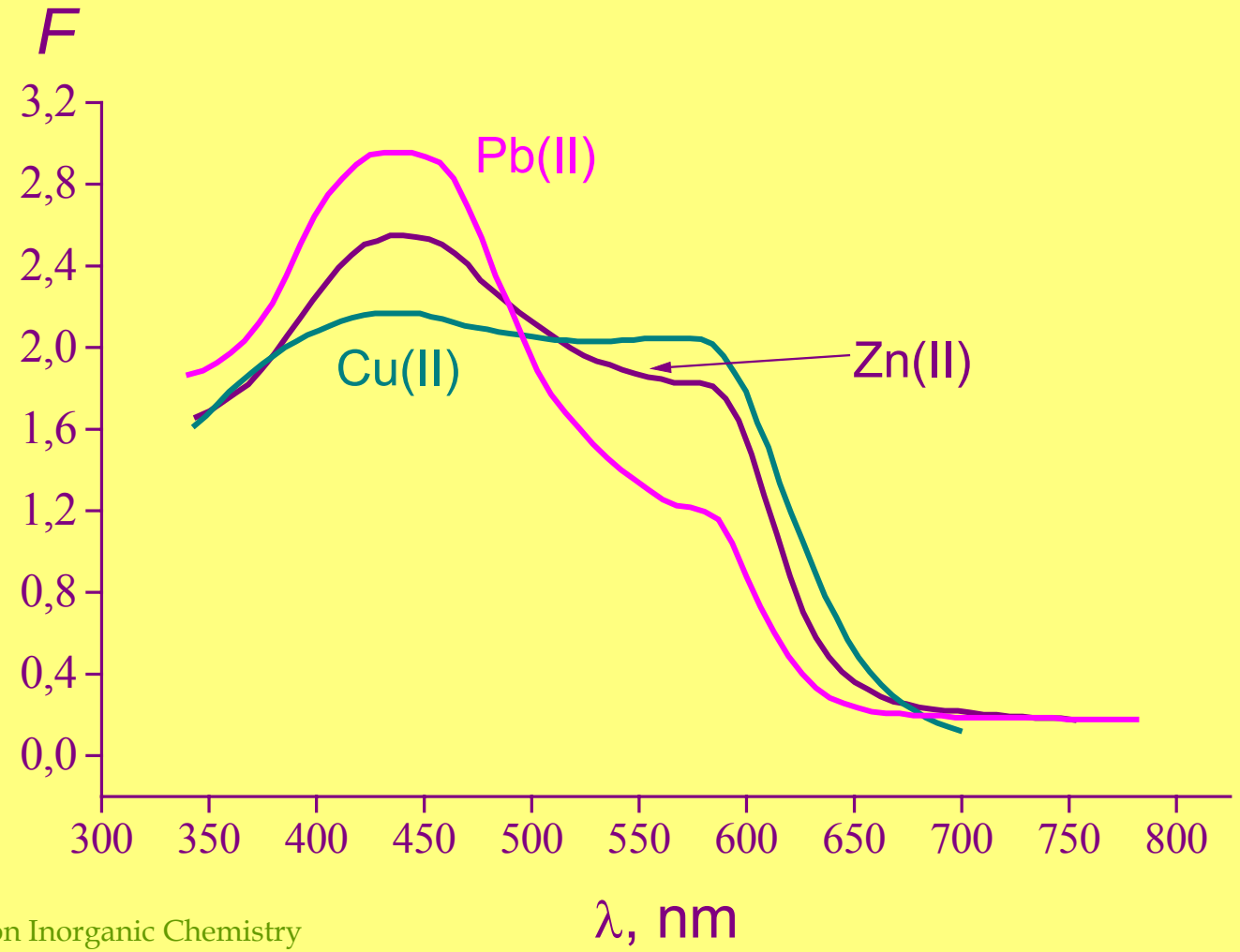
pH > 6.5
H_2L^{4-}
570–580 nm



Absorption spectra of metal ion complexes with immobilized xylenol orange

Aqueous solutions:

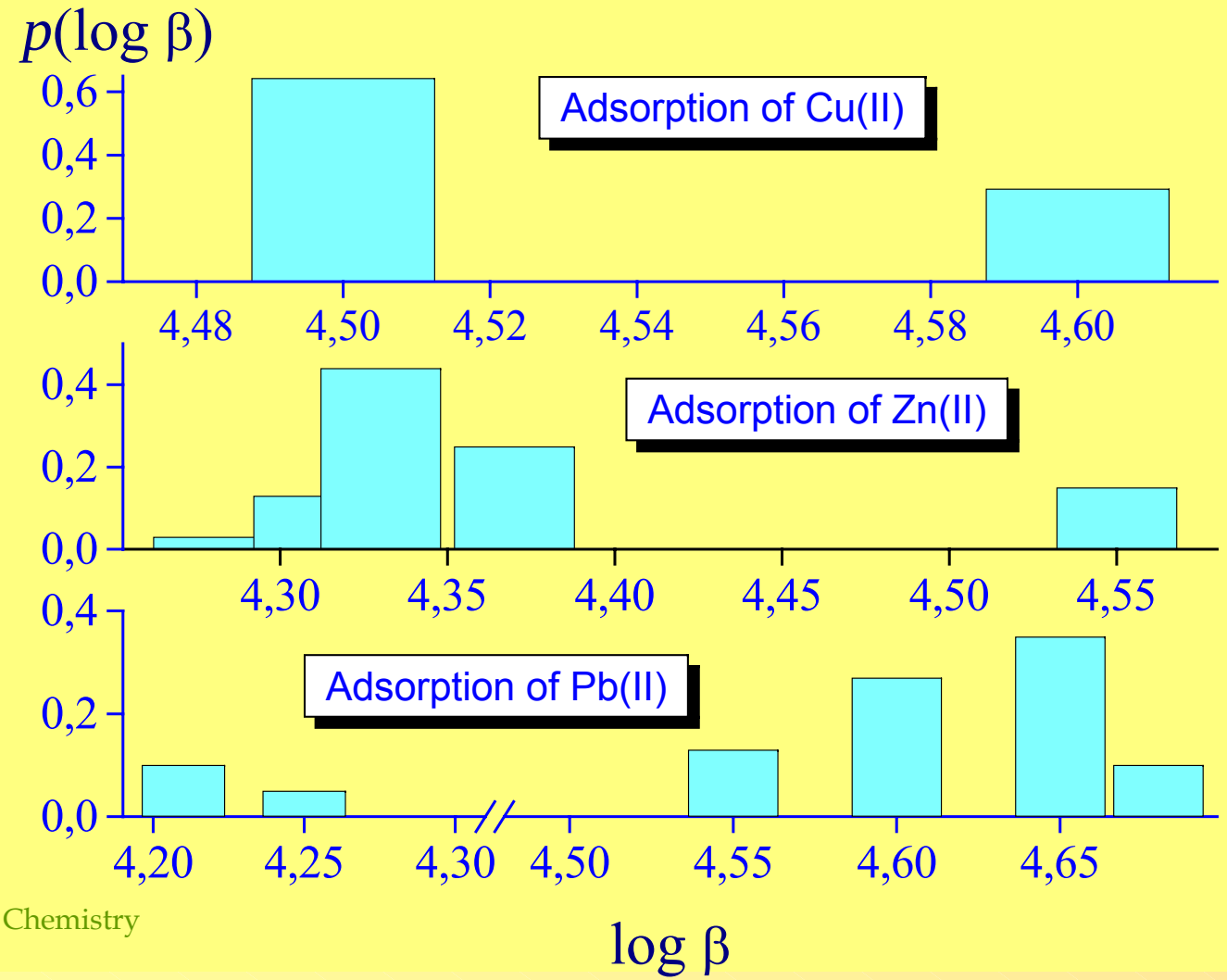
at pH 5-7:
λ_{max} =
570–580 nm



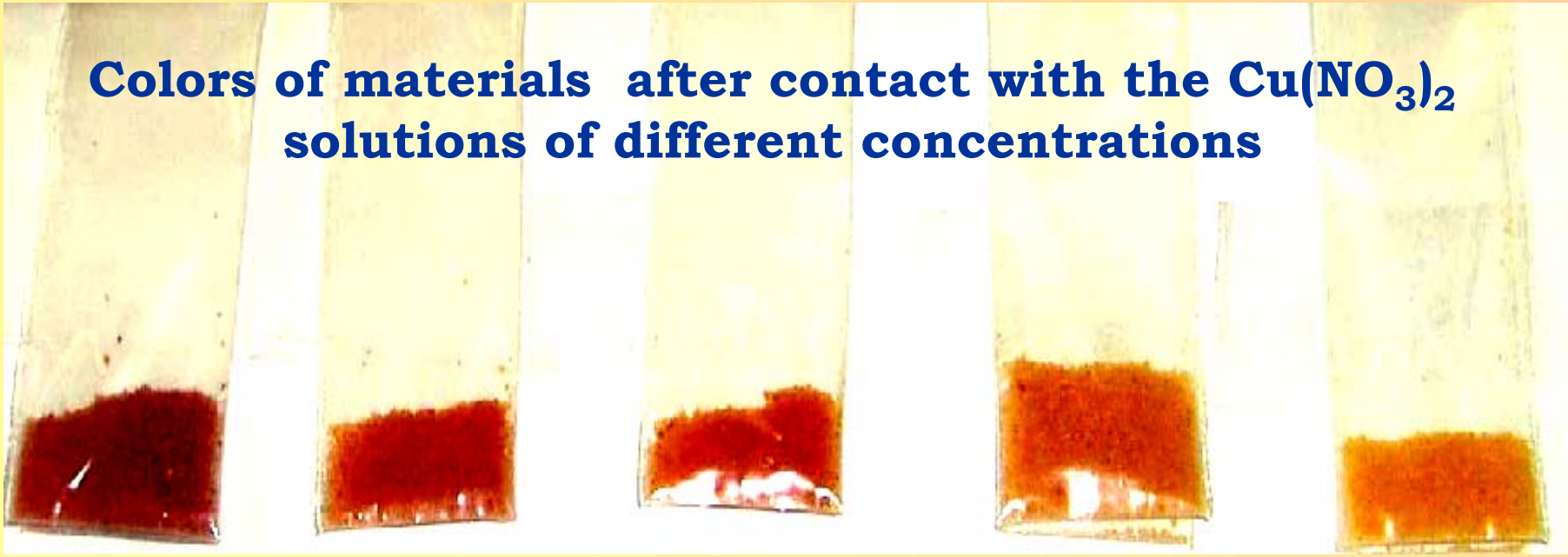
Distributions of sorption centers in affinity to metal ions

Xerogel – xylenol orange

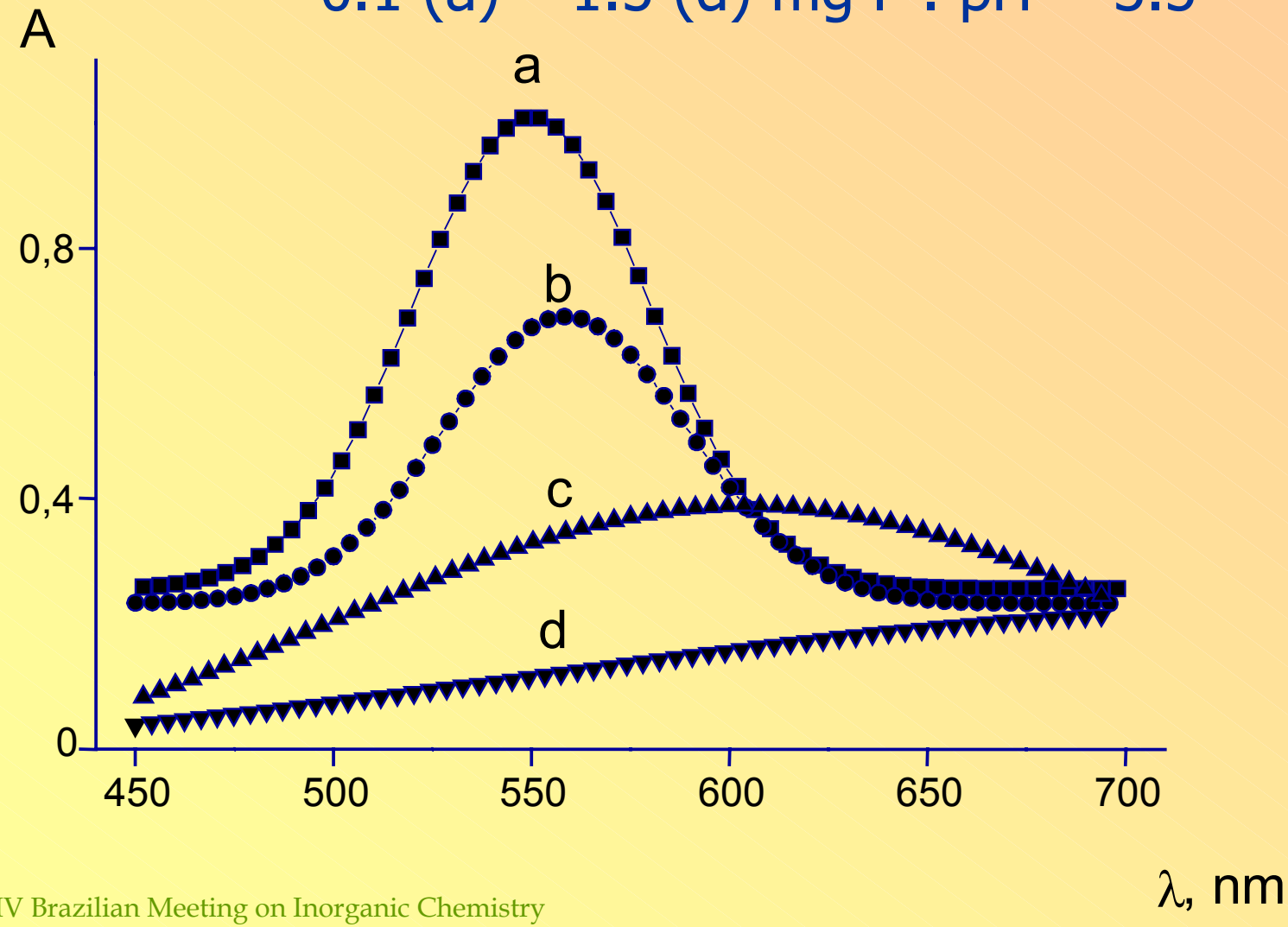
pH 5.6-5.8



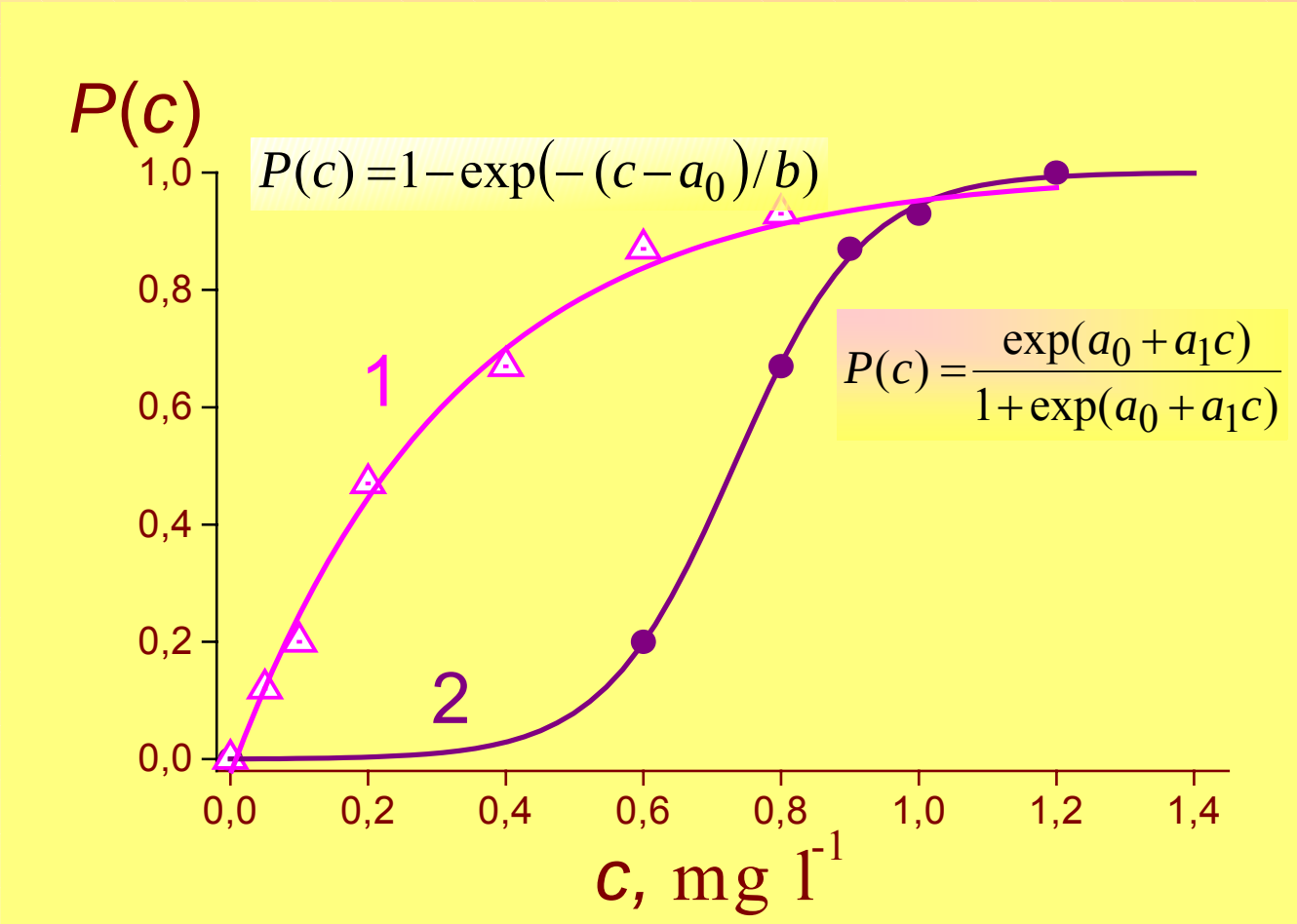
Visual test detection and semiquantitative determination of metal ions with the aid of xerogel with immobilized xylenol orange



Fluorescence quenching of immobilized calcein at Cu(II) concentrations in solutions: 0.1 (a) – 1.5 (d) mg l^{-1}. pH = 3.5



Performance characteristic curveы for detection of Cu(II) (1) and sum of equal mass concentrations of Cu(II), Zn (II) and Pb(II) (2)



1: xerogel with calcein (0.7_μmol g^{-1}),
2: xerogel with xylenol orange (35 μmol g $^{-1}$).

Metrological characteristics for procedures of visual detection of metal ions

Material	Sorbate	Unreliability interval, mg l^{-1}	Detection limit, mg l^{-1}
Xerogel – xylenol orange	Cu(II)	0.2 – 0.7	0.7
	Zn(II)	0.2 – 0.7	0.7
	Pb(II)	1.2 – 1.9	1.9
	Cu(II) + Zn(II)+ + Pb(II)	0.4 – 1.0	1.0
Xerogel – calcein	Cu(II)	0.02 – 1.0	1.0

Acknowledgements

Colleagues in Ukraine
Dr Sergiy Myerniy
Prof Valentin Tertykh

Colleagues in Brazil
Prof Yoshitaka Gushikem
Mr. Fabio Pissetti

Thank you!