

Exercise 3

Polymeric Materials

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Ion exchange in separation processes

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Requirements:

1. Calculation and re-calculation of concentrations
2. Ion exchange resins, ion exchange
3. Principle of ion exchange process

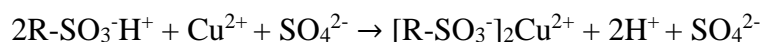
Ion exchangers, or as they are often called ionites, are solid, insoluble polyelectrolytes characterized by the ability to exchange ions attached to their functional groups to ions located in the external solution.

Polymers with ion-exchange functional groups are divided into two groups:

- a) **Cation exchange resins**, possessing groups revealing characteristics of an anion: -SO₃H, -PO₃H, -COOH
- b) **Anion exchange resins**, possessing groups revealing characteristics of a cation: -NR₂H, -N⁺R₃

This means that the polymer in which the functional groups are capable of binding anions is called anion exchange resin (e.g., a polymer with amino groups), and the polymer in which the functional groups are capable of binding cations is called a cation exchange resin (a polymer with carboxyl or sulphonic groups).

During the ion exchange, a cation exchange resin, initially in the acid form, passes into the corresponding salt according to the reaction:



A cation exchange resin, which is transformed into a salt form, can be completely regenerated using acid, and an anion exchange resin can be regenerated with a hydroxide. The ion exchange process is an equilibrium process, and the phenomena occurring during the exchange take place at the interface between the solid and the water phase.

Ion exchange processes are used in water treatment processes: for drinking water treatment, water desalination and softening, for technological water purification, e.g. in power plants, and in hydrometallurgical processes for metal recovery, among others, precious metals

The aim of the exercise is to separate ions of copper(II) using strong-acidic cation exchange resin with sulphonic functional groups. To do so it is necessary to:

1. Prepare 1L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (4 gL^{-1}) solution
2. Prepare calibration curve of Cu(II). Dilute solution prepared in point 1 in a way allowing to receive following concentrations of copper sulphate: 2, 1, 0.5, 0.25, 0.125, 0.05 and 0.025 gL^{-1} . Next, using portable colorimeter, draw curve $\Delta E = f(C)$ and determine linear range thereof.
3. Wash the bead of cation exchange resins (placed in a column) with water and 1M HCl. Using a tap, adjust flow rate.
4. Measure the height and diameter of the resin bead before concentration of copper. Thickness of the walls of glass ion exchange column is 2 mm. Measure the resin bead again after concentration of Cu(II) and after regeneration as well.
5. Introduce into the column solution prepared in point 1.
6. Collect the passed solution in 25 mL portions. Measure change of a colour by determining value of ΔE using colorimeter.
7. The resin becomes fully saturated when to colour of solution collected at the bottom of the column matches the feed solution. After reaching thereof, wash the resin with water.
8. Regenerate the resin using 1M HCl. Measure value of ΔE for the collected solution.
9. Wash the resin with water

Preparation of the results:

1. Plot the calibration curve. Approximate linear area with a suitable function.
2. Calculate initial volume of the resin bead (BV_s).
3. Calculate sorption of Cu(II) for each portion of the collected solution using following equation:

$$S = \frac{(C_p - C_K) \cdot K}{BV_s} \quad \left[\frac{\text{mg}}{\text{mL}} \right]$$

Gdzie: C_p -initial concentration; C_K -final concentration; K-propotion coefficient; BV_s -volume of resin bead.

4. Calculate total capacity of the resin.
5. Plot breakthrough curve $\frac{C_K}{C_p} = f(BV_s)$
6. Propose a method for calculating yield (%) of regeneration.

Colorimetry

The word *colour* has double meaning: on the one hand it describes quality feature of an object, and on the other, esthetic impression of a viewer. The perceived colours are described by unique words, as blue, green, yellow, etc. These, in turn, cannot be defined using other words as they are considered as representation of fundamental concepts. Therefore, visual experience correlated with colours strongly depends on each individual observer making their perception as diversified as it can possibly be [1]. For that reason, it was necessary to introduce proper standards and procedures being able to represent colour as numeric values; to make it happen, understanding how a human eye recognizes a colour is necessary.

The theories describing experience of an colour state, that its perception depends on three main factors:

- 1) **Hue/tint**, defined by wavelength of electromagnetic radiation (packages of photons) reflected from, or transmitted through an object.

Human eye is able to detect electromagnetic radiation in range of 380-780 nm (visible light spectrum). If the colour of a non-transparent object is recognized as green, it means that its surface **reflects** wave light characterized by 500-560 nm wavelength, absorbing rest of the spectrum (Figure 1). On the other hand, if the same colour is observed in case of a transparent object, it means that it **transmits** the same wave light, absorbing rest of the spectrum.

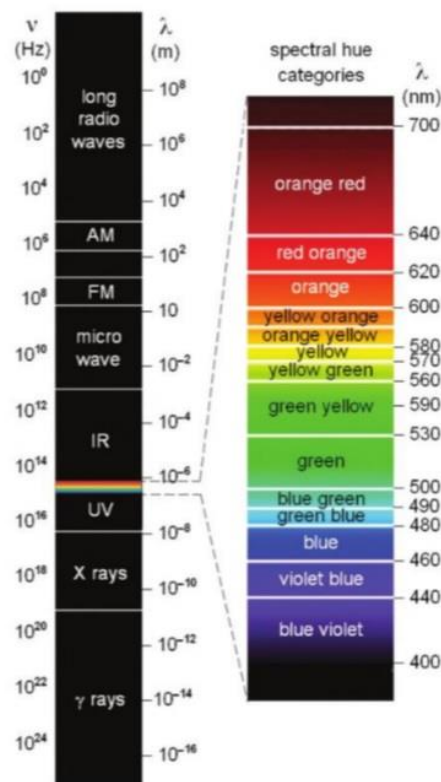


Figure 1. Spectrum of electromagnetic radiation characterized as wavelength [1]

- 2) **Chroma/Saturation**, defining if a color is monochromatic, or, using other words, how vivid or faded a colour is. Monochromatic ones are the most saturated, the most vivid; non-monochromatic in turn, are close to gray, being faded.

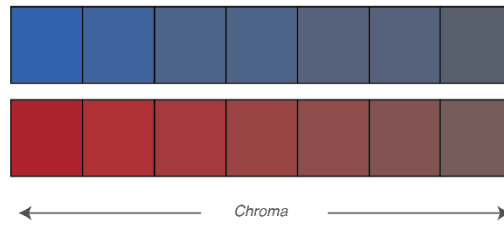


Figure 2. Chroma of blue and red colours [2]

- 3) **Brightness** defined by amount of the reflected/transmitted light; determines experience correlated with dark or bright colours

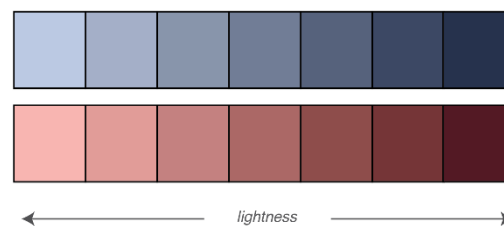


Figure 3. Brightness of blue and red colours [3]

Moreover, experience of a colour is also dependent on variables not directly linked to hue, saturation and brightness. These are:

- 1) **degree**, at which a virtual observer is experiencing a colour (value called *standard observer*)
- 2) **type of the light** illuminating an observed object; we can distinguish the following types of illuminants [4]:
 - a. **A**, domestic light induced by tungsten filament with correlated colour temperature (CCT) of 2856K
 - b. **B**, daylight, CCT=4874K
 - c. **C**, daylight, CCT=6774K
 - d. **D**, daylight at variable CCT
 - e. **E**, illuminant with controlled distribution of the visible spectrum, gives equal energy for all wavelengths
 - f. **F**, fluorescent illuminants

Because humans' perception of a colour is dependent on the mentioned above variables, a final model describing its parameters must be 3-Dimensional, which complicates the whole matter. Common colour systems, used for instance in computer displays (RGB- *Red Green Blue*) or printing devices (CMYK-*Cyan Magenta Yellow Black*) are very important from practical point of view, however they are not sufficient as precise description of an colour, expressed in 3D system [1]. One of the first systems taking into account 3D position of an colour as a function of hue, saturation and brightness was introduced by Munsell in 1900s [4]

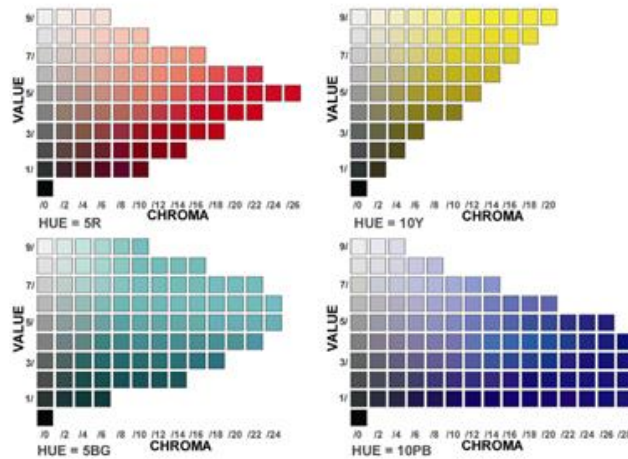


Figure 4. An example of Munsell system for four different hues [4]

Despite its advance at the time, the main practical disadvantage of the Munsell colour system is that the colours are defined only for one *standard observer* (2°) and only for one type of light illuminating an object (C). For that reason it was necessary to develop more advanced model.

Nowadays the most popular colour system, used in various types of industries is CIE $*L^*a^*b^*$ space created by International Commission on Illumination. This system is reflecting how a human's eye recognizes differences between colours and assumes, that difference between them is linear, opening the path for colorimetric analysis.

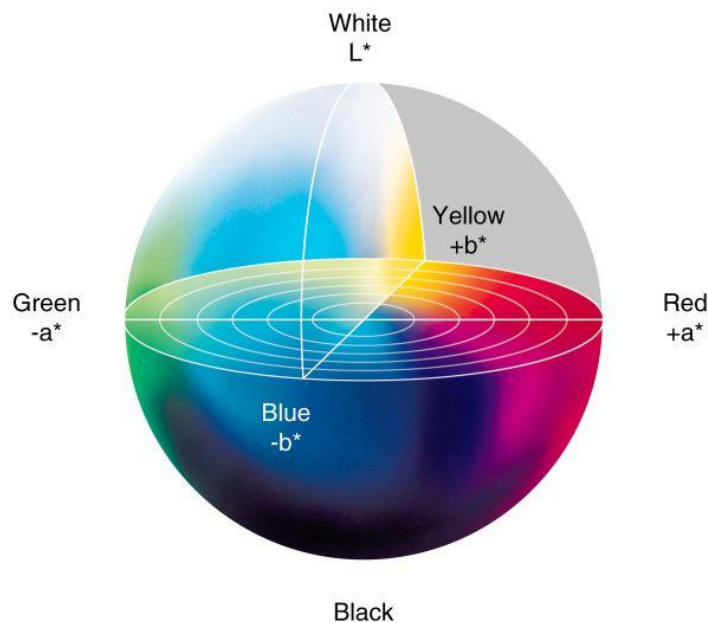


Figure 5. CIE $*L^*a^*b^*$ space [5]

The system CIE $*L^*a^*b^*$ is defined by three parameters:

- 1) **L**: light versus dark, the lower number is, the darker colour is observed
- 2) **a**: red versus green, where positive values means red, negative, in turn, green
- 3) **b**: yellow versus blue, where positive values means yellow, negative, blue

The *L*a*b parameters are linked to each other by cube root function, which means, that creating an analytical curve in this 3D system (Figure 5) would require usage of complicated equations and specific software able to create visual representation of the collected data. However, the major advantage of CIE *L*a*b system is the possibility of determination of difference between colors expressed as numeric value ΔE . This parameter is defined as:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad (1)$$

Because of the fact, that ΔE changes proportionally with actual change of the observed colors it is possible to transfer *L*a*b parameters into 2-dimensional system expressed as $\Delta E=f(C)$, where color is a function of concentration (C).

[1] C. Oleari, *Standard Colorimetry: Definitions, Algorithms and Software*, John Wiley&Sons, Chichester, 2016

[2] website: <http://blogs.adobe.com/creativecloud/files/2014/06/TenWays-chroma.png>, access date: July 14th, 2016

[3] website: <http://blogs.adobe.com/creativecloud/files/2014/06/TenWays-lightness.png>, access date: July 14th, 2016

[4] D. Malacara, *Color Vision and Colorimetry: Theory and Applications, Second Edition*, SPIE Press, Bellingham, 2002

[5] website: http://www.coatsindustrial.com/pl/images/Colour%20difference_tcm81-152855.jpg, access date: July 14th, 2016

[6] R.F. Witzel, R.W. Burnham, J.W. Onley, *Threshold and suprathreshold perceptual color differences*, J. Optical Society of America 63, 615-625, 1973