Absorption spectroscopy

Metal ions

Assays

Matrix solutions

Fundamentals of the extinction coefficient The absorption cross section, σ_{A}

The absorption cross section has units of area (cm²). It gives a probability for absorption. We have discussed the probability in terms of the transition dipole moment. M_{12} and shape in terms of the Franck-Condon factor, FC.

 $\sigma_{\!A}(\omega) \propto |M_{12}|^2 FC(\omega)$

The absorption cross section is proportional to the well known extinction coefficient.

$$\epsilon(\omega) = \frac{\sigma_A(\omega)N_A}{1000}$$

The extinction coefficient has units of M⁻¹cm⁻¹.

Beer-Lambert Law

$$I = I_0 10^{-A}$$

 $A = \epsilon(\lambda) c d$

A is the absorbance. $\varepsilon(v)$ is the extinction coefficient. The unit of $\varepsilon(v)$ is M⁻¹cm⁻¹. c is the concentration (M). d is the pathlength (cm). The exponential attenuation of the intensity is shown in the Figure.



Neodymium spectroscopy: forbidden f-f transitions

The ground state electron configuration of Nd is [Xe]4f⁴6s². However, Nd(III) has a configuration [Xe]4f³. Nd transitions observed in the absorption spectrum start from the ⁴I_{9/2} ground state. Transitions to the following σ-polarization 4G ... +2G ... 2 S+ 1 L₁ levels can be observed: 4 F_{3/2}, 2 H_{9/2}, Absorption coefficient, cm⁻¹ ⁴F_{5/2}, ⁴F_{7/2}, ⁴S_{3/2}, ⁴F_{9/2}, ²H_{11/2}, ⁴G_{5/2}, ²G_{7/2}, ⁴G_{7/2}, ⁴K_{13/2}, ⁴G_{9/2}4, ²K_{15/2}, ⁴G_{11/2}, ²D_{3/2} π-polarization and ${}^{2}G_{9/2}$. The spectrum shown is a high resolution spectrum of Nd-doped LaTiO₃.

600

Wavelength,nm

800

500

Neodymium spectroscopy: expanded view



Copper sulfate spectroscopy: forbidden d-d transitions

The ground state electron configuration of Cu is [Ar]3d¹⁰4s¹. However, Cu(II) has a

configuration [Ar]3d⁹. In the hexahydrate there is an octahedral ligand field. It is an

Unusual case because the water molecules all have the same Cu-O bond length.

Copper (II) Sulfate There is no measurable Jahn-Teller distortion. The electronic transition is LaPorte forbidden. 1.0 Absorbano d-d transitions are broad. 0.5

Problem in linear analysis using analytical chemistry

A student determines absorbance of a solution known to contain 4 strongly absorbing dyes (labeled dye A, B, C and D) at four different wavelengths $\lambda = 495,420,470$ and 590 nm. The extinction coefficients $\varepsilon_{\lambda}(dye)$ for the 4 compounds at these 4 wavelengths are known (units lit/mol):

	A	В	C	D
8 ₃₉₅	13500	2000	28000	7200
ε ₄₂₀	180000	4500	14000	8000
ε ₄₇₀	700	700	3000	32000
ε ₅₉₀	8000	70000	400	1350

Problem in linear analysis using analytical chemistry

The absorbance values in a 1 cm pathlength are:



What are the four concentrations?

(*Hint*: Absorbance A= ε_{λ} Lc is an additive quantity, so you can write out the problem as a set of linear equations. Then write this as a matrix formula and see if you can solve it by matrix algebra.

Method using matrix analysis

The equations have the form

$$A_{1} = \varepsilon_{11}c_{1} + \varepsilon_{12}c_{2} + \varepsilon_{13}c_{3} + \varepsilon_{14}c_{4}$$

$$A_{2} = \varepsilon_{21}c_{1} + \varepsilon_{22}c_{2} + \varepsilon_{23}c_{3} + \varepsilon_{24}c_{4}$$

$$A_{3} = \varepsilon_{31}c_{1} + \varepsilon_{32}c_{2} + \varepsilon_{33}c_{3} + \varepsilon_{34}c_{4}$$

$$A_{4} = \varepsilon_{41}c_{1} + \varepsilon_{42}c_{2} + \varepsilon_{43}c_{3} + \varepsilon_{44}c_{4}$$

We can write these compactly in matrix form as:

$$A = \varepsilon c$$

Where the knowns are the vector A of absorbances and the matrix of the extinction coefficients. We can solve for the concentrations using the matrix inverse:

$$\varepsilon^{-1}A = \varepsilon^{-1}\varepsilon c$$

Which tells us that

$$c=\varepsilon^{-1}A$$

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