L

[illegible]

Análise Quantitativa

⇒ Espécie a ser analisada deve absorver luz em λ conhecido

⇒ λ de absorção deve ser diferenciado de outras substâncias presentes na amostra

Ex: Análise de Fe^{2+} (incolor) em amostra desconhecida

$Fe^{2+} + 3\ \underbrace{\text{ferrozina}^{2-}} \Rightarrow (\text{ferrozina})_3Fe^{4-}$

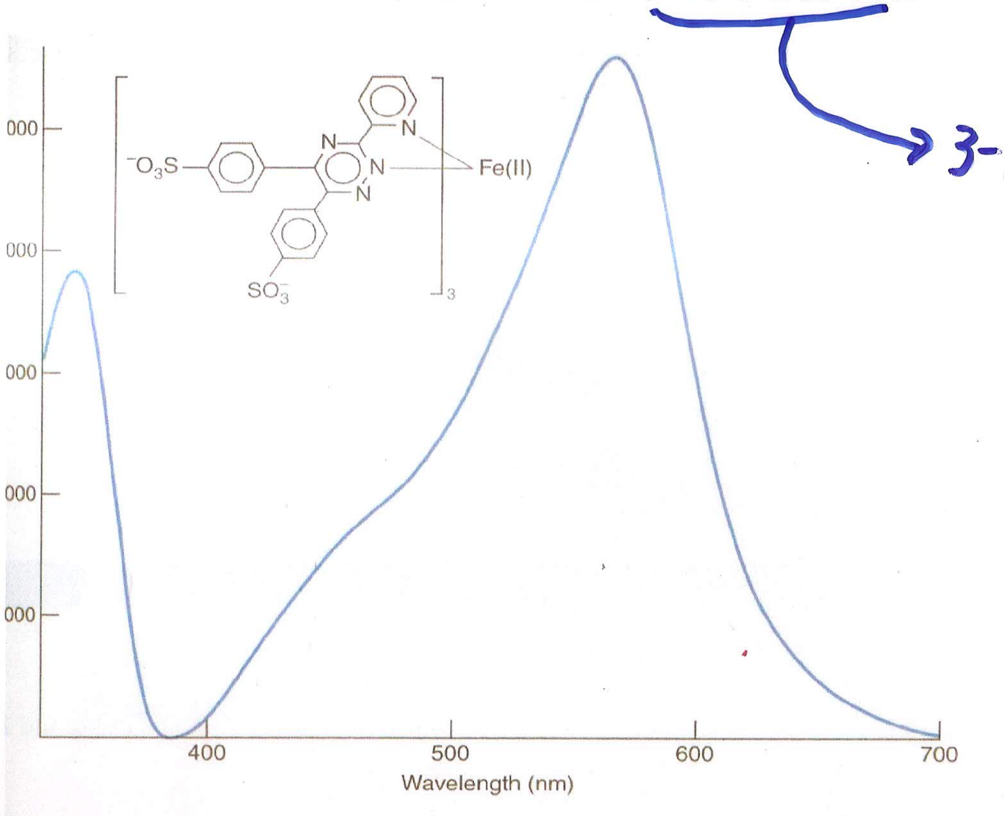
λ max. = 562 nm

→ 3-(2-Piridil)-5,6-bis(4-fenilsulfônico ácido)-1,2,4-triazina

≠ ferroína

o-ph / Fe(II) complexo

~ 510nm



30

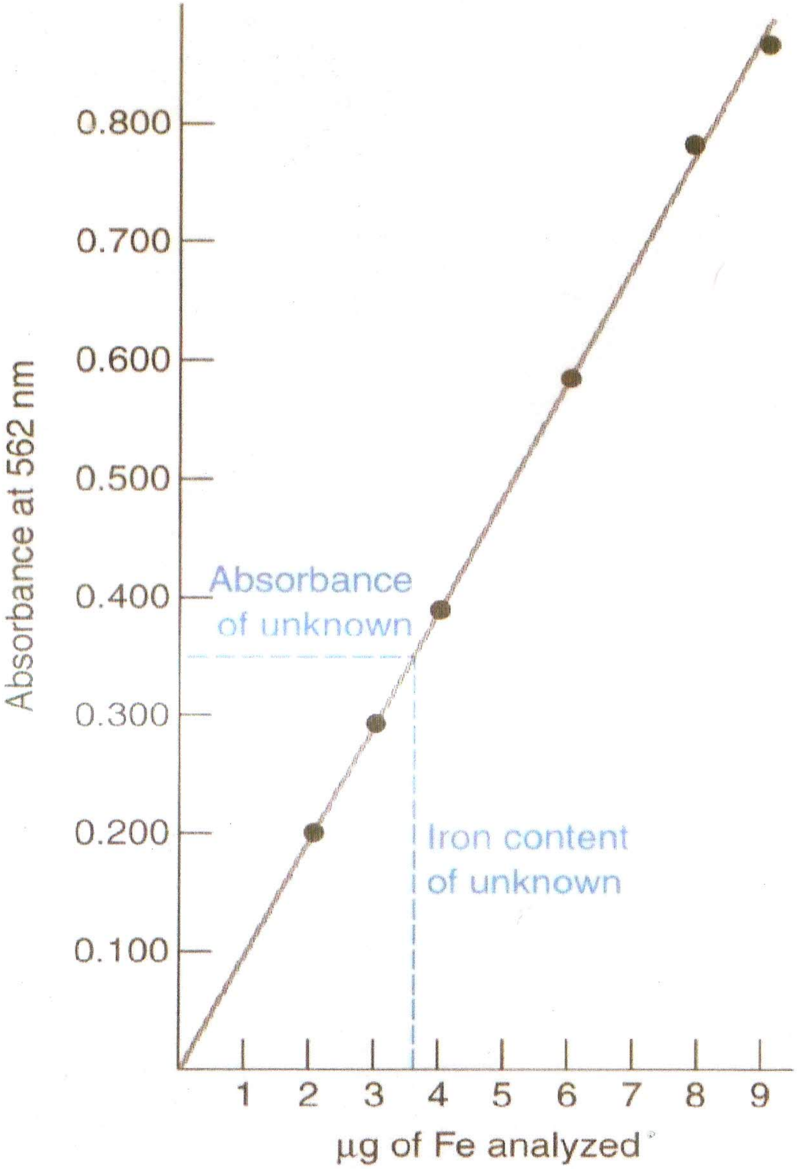
1. Preparo de um "branco"

⇒ contém todos os reagentes presentes na solução da espécie a ser analisada, ***menos*** a espécie a ser analisada

⇒ subtrai-se Absorbância do branco da Absorbância da amostra antes de realizar-se os cálculos

2. Construção da curva de calibração

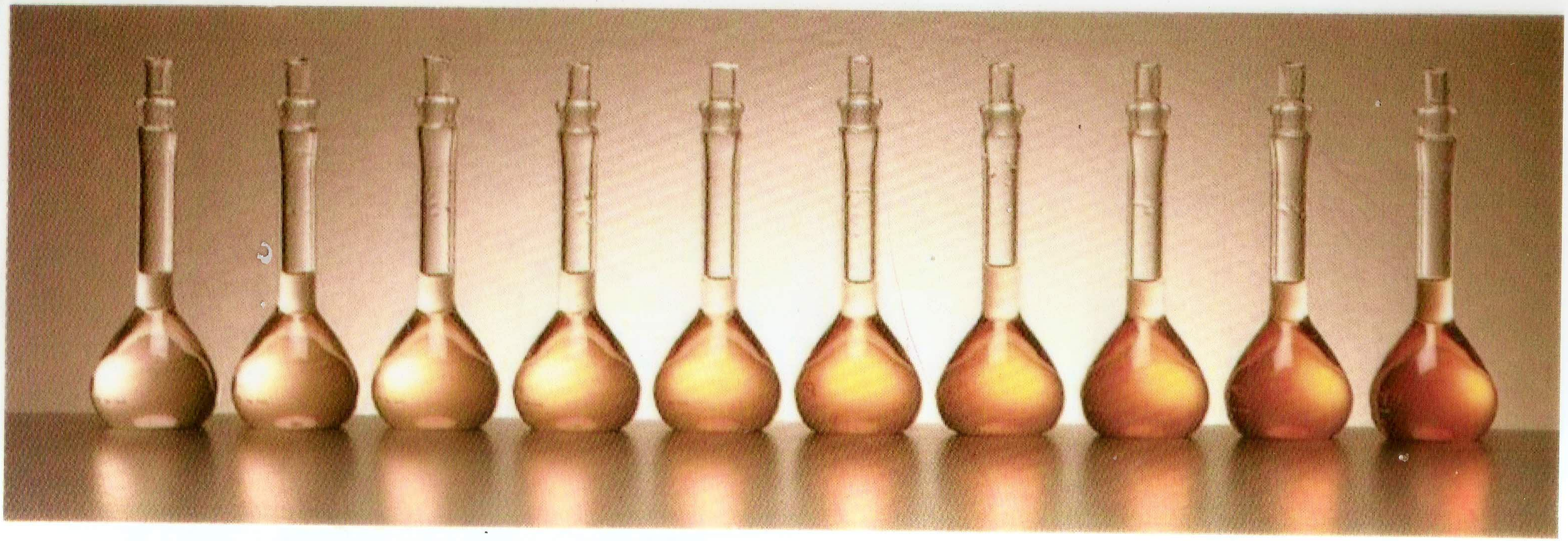
⇒ medida da absorbância de várias soluções de concentração conhecida da espécie a ser determinada



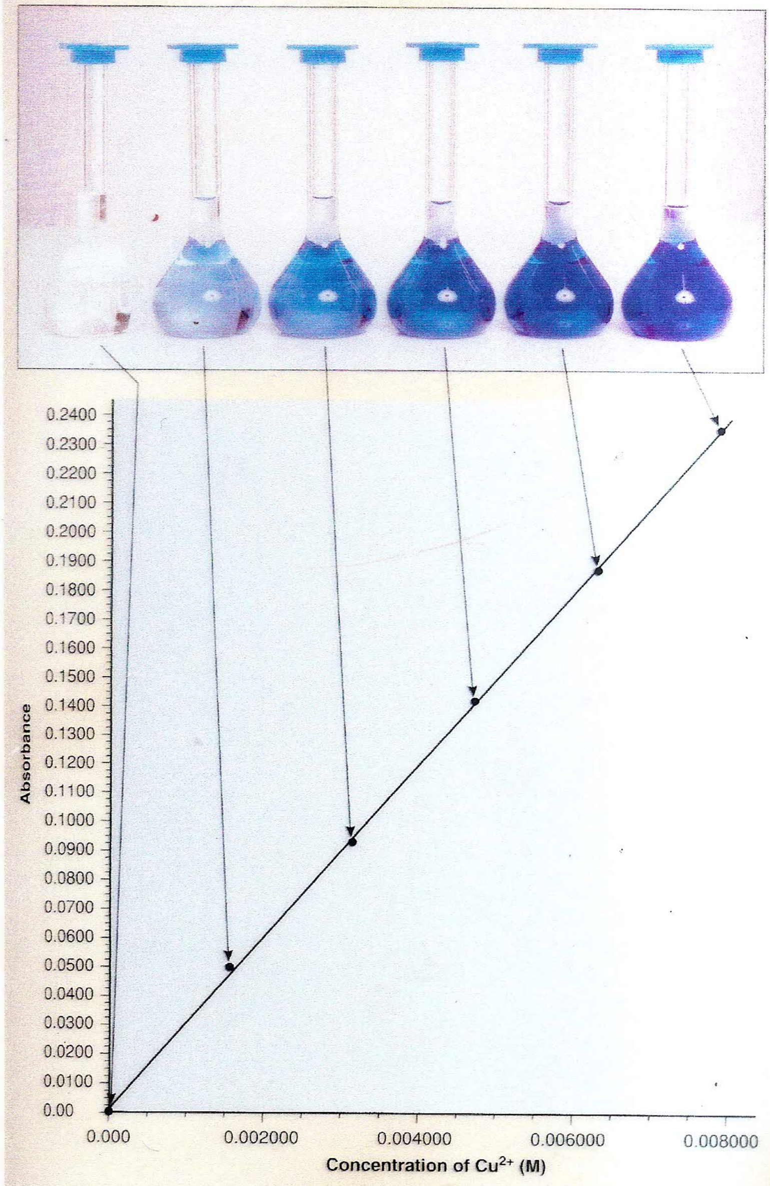
L

3

L



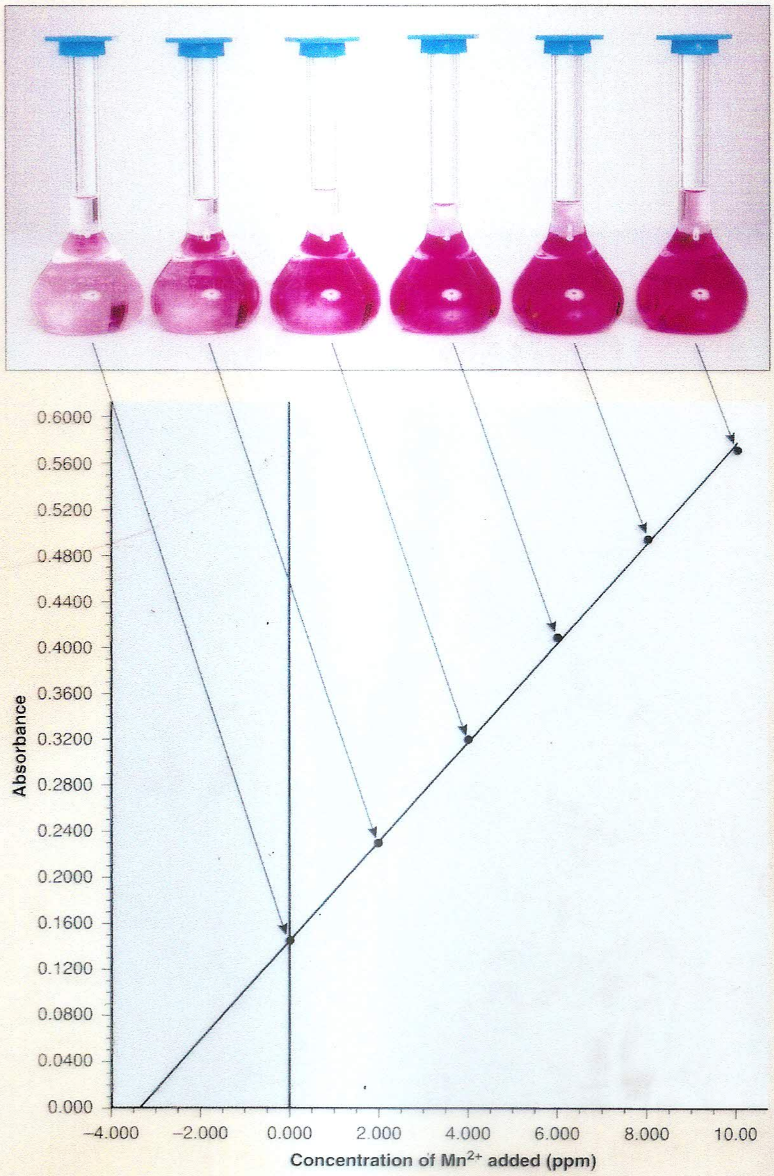
COLOR PLATE 13 **Beer's Law (Section 19-2)** Fe(phenanthroline)$_3^{2+}$ standards for spectrophotometric analysis. Volumetric flasks contain Fe(phenanthroline)$_3^{2+}$ with Fe concentrations ranging from 1 mg/L (left) to 10 mg/L (right). The absorbance, as evidenced by the intensity of the color, is proportional to the iron concentration.



Colorplate 1

A set of external standards for Cu^{2+} showing the associated calibration curve.

L



Colorplate 2
A set of standard additions for the determination of Mn^{2+} showing the associated calibration curve.

SÉRIE DE ADIÇÕES PADRÃO

33

L

100% T. Then the solvent is replaced by the solution and the transmittance read. This process is repeated at, say, 410, 420, 430, ... mμ. The interval between the wavelength settings need not be constant; indeed, the values selected will depend on the shape of the curve and the degree to which finer details of the curve must be secured. The values of % T found are plotted versus the wavelength values and a smooth curve is drawn through the points. Either by substitution in the formula $A = -\log T$ or by reading the absorbance scale provided additionally on most instruments, the corresponding absorbance values are obtained and plotted versus the wavelength values to obtain the absorbance curve. A typical transmittance curve and its equivalent absorbance curve are shown in Figure 36-2.

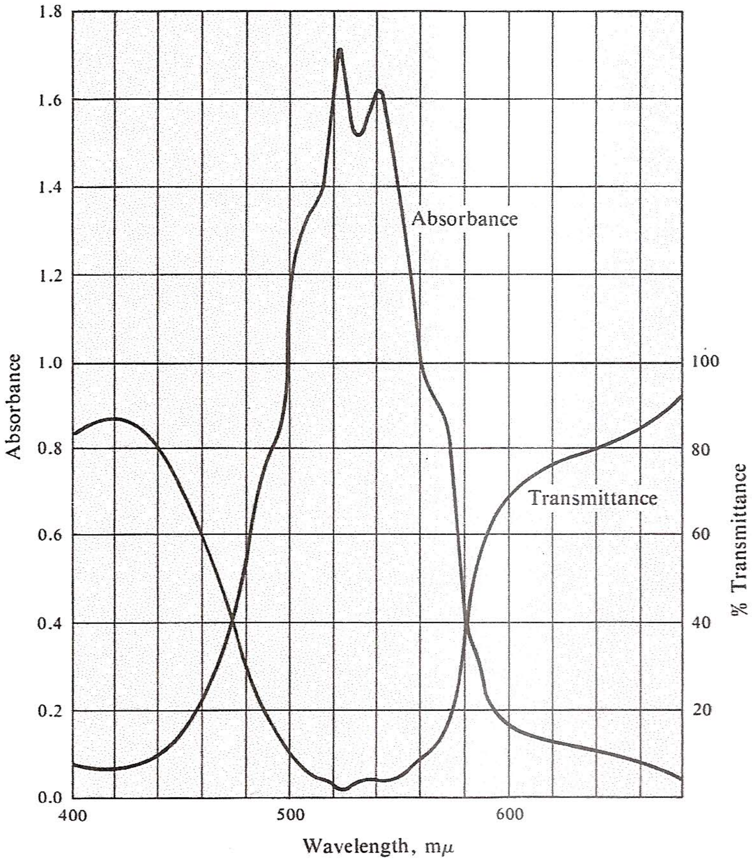
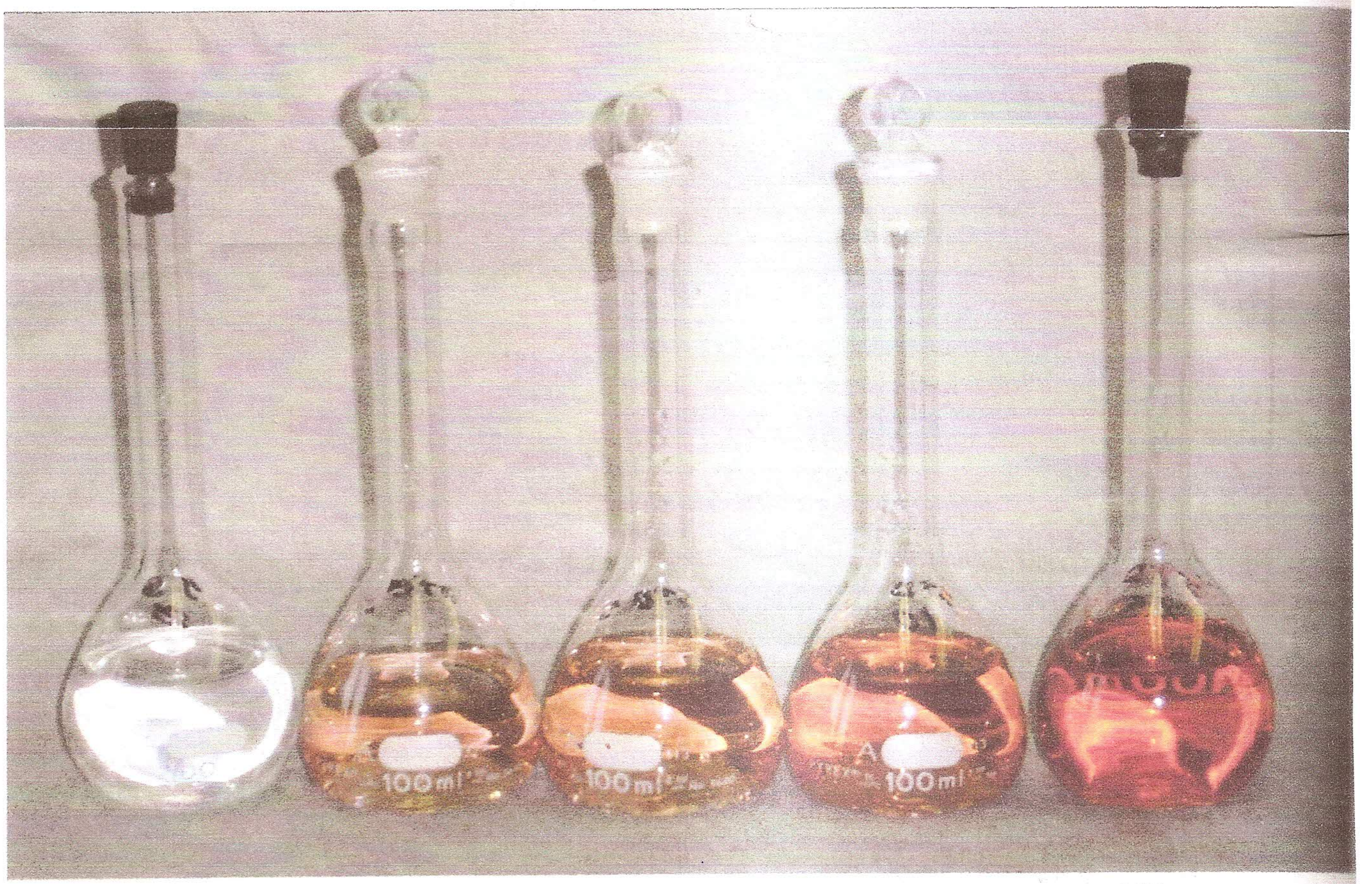


Figure 36-2. Absorbance and transmittance curves for $KMnO_4$ in water (40 mg/liter, 1-cm cell) for the region 400 to 680 mμ.

0,00025 M = 0,25 mM = 40 ppm sal = 14 ppm Mn

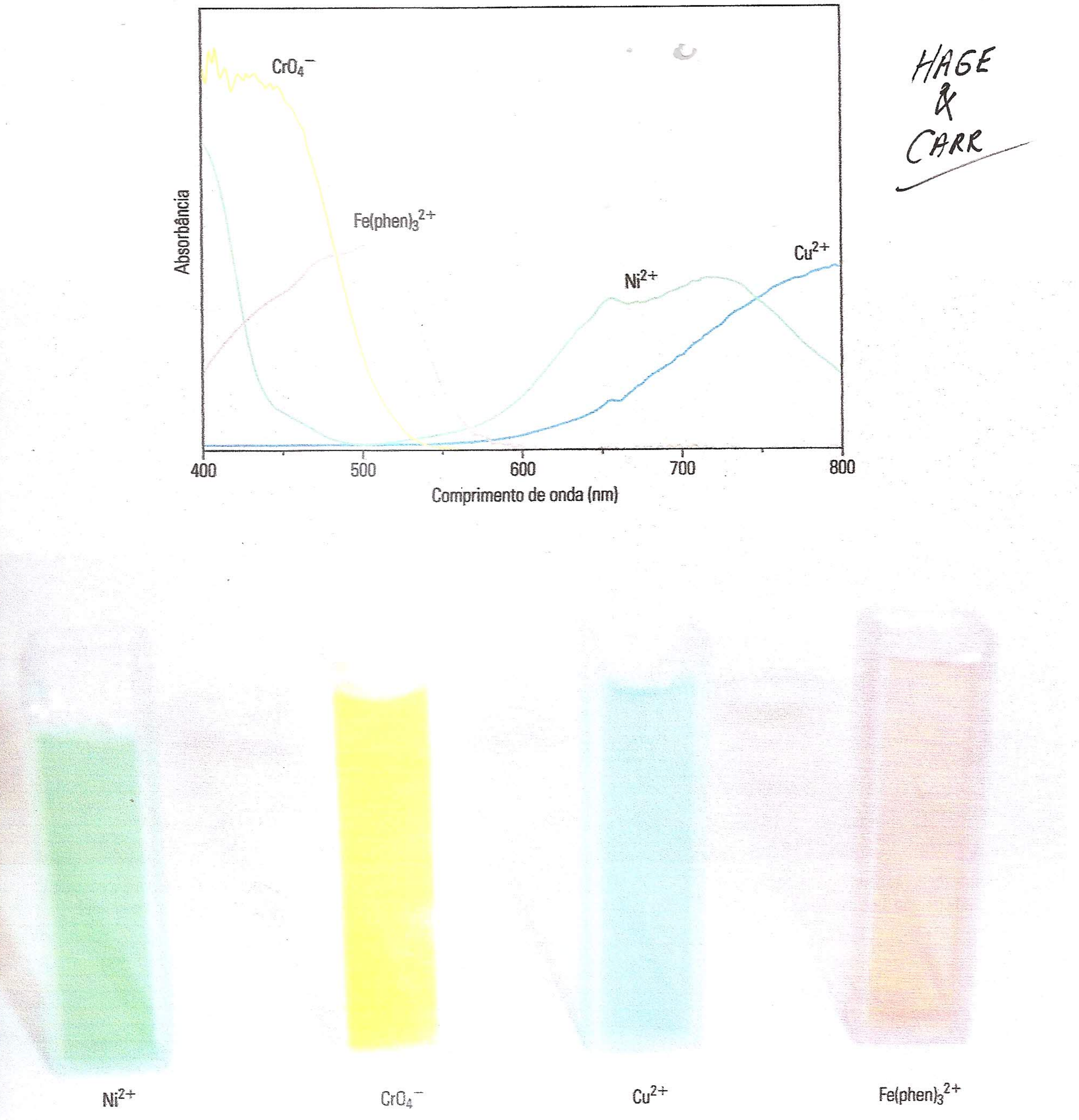
$Fe^{2+} + 3\ phen \longrightarrow Fe(phen)_3^{2+}$



Conc. Fe^{2+}:	0,000 ppm	0,359 ppm	0,599 ppm	1,198 ppm	2,995 ppm
Abs. (510 nm):	0,004	0,084	0,133	0,264	0,640

Soluções-padrão para a determinação espectrofotométrica de Fe^{2+} por meio de sua reação com 1,10-fenantrolina (phen) para formar um complexo colorido. As soluções nesses balões volumétricos foram preparadas para conter um excesso de 1,10-fenantrolina como agente complexante para Fe^{2+} e agente de formação de cor. Os balões também continham hidroxilamina (agente redutor que evita a oxidação de Fe^{2+} a Fe^{3+}) e acetato de sódio como tampão. A concentração final de Fe^{2+} em cada um dos padrões é mostrada no topo. Os valores de absorbância medidos em 510 nm para as soluções-padrão são listados na parte inferior. Outros exemplos desses ensaios podem ser encontrados no Capítulo 18.

HAGE
&
CARR



Exemplos de como a cor observada em uma solução química está relacionada ao espectro de absorção dessa solução na faixa de comprimento de onda visível. Os recipientes na parte inferior são cubetas de 1,0 cm que contêm soluções aquosas de Ni^{2+} (verde), CrO_4^{2-} (amarelo), Cu^{2+} (azul) ou $Fe(phen)_3^{2+}$ (laranja). Os espectros de absorção correspondentes a essas soluções são mostrados no topo. Essa comparação ilustra como a cor observada das soluções está relacionada aos comprimentos de onda da luz visível que não são absorvidos, mas transmitidos através das soluções. Esse efeito é discutido com mais detalhes no Capítulo 17.

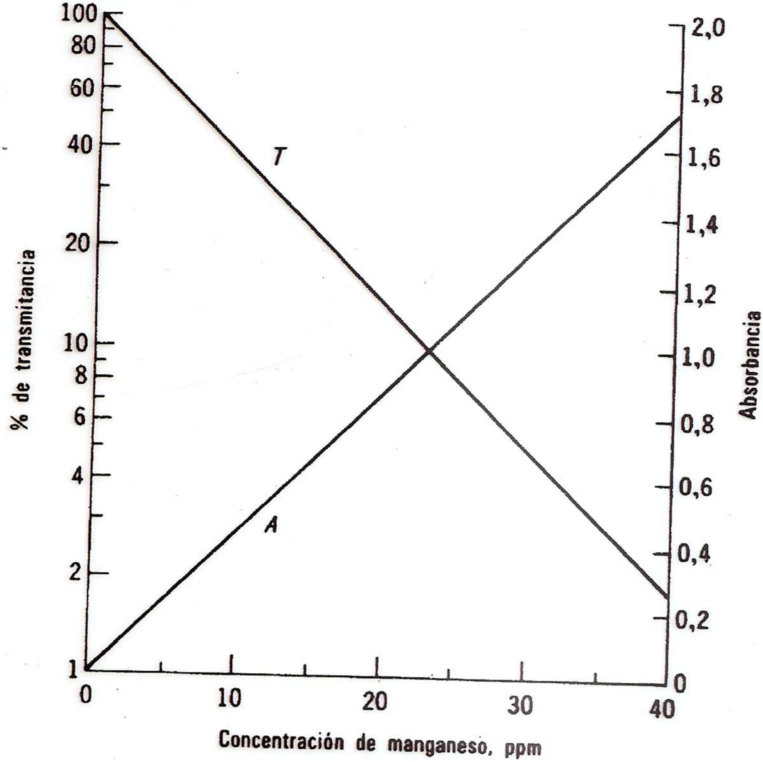


Fig. 31-11 Curvas patrón de disolución de permanganato, medidas a 526 mμ en células de 1,00 cm.

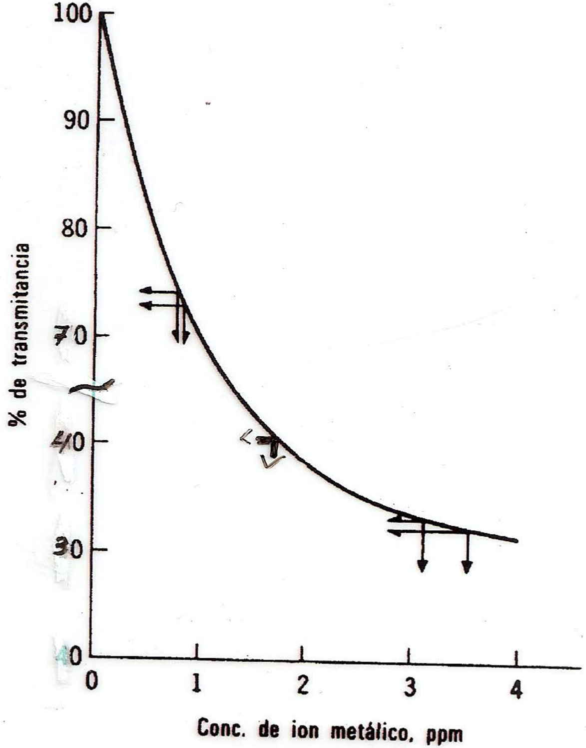


Fig. 31-10 Curva de calibración transmitancia-concentración.

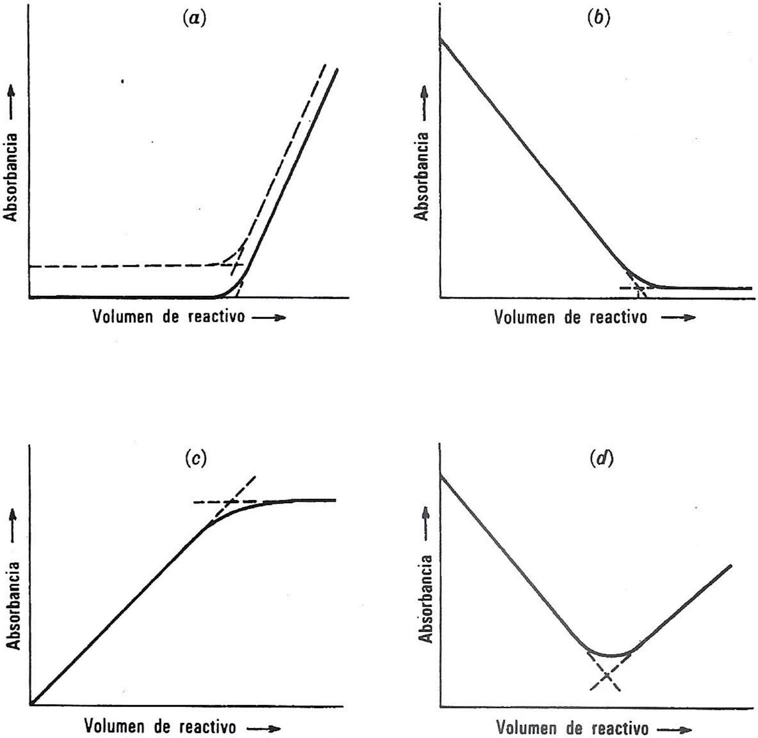


Fig. 31-22 Curvas de valoración fotométrica. Reacción: X + Y (reactivo) → Z. (*a*) Y absorbe, X y Z no. (*b*) X absorbe, Y y Z no. (*c*) Z absorbe, X e Y no. (*d*) X e Y absorben, Z no.

Aparelho melhor...

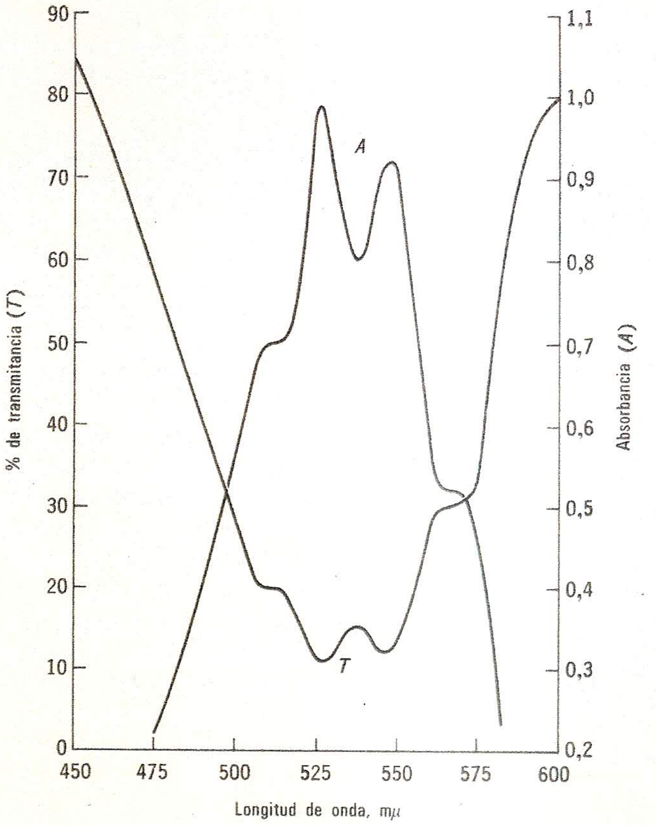


Fig. 31-9 Curvas espectrales de una disolución de permanganato potásico que contiene 20 ppm de manganeso.

100% *T*. Then the solvent is replaced by the solution and the transmittance read. This process is repeated at, say, 410, 420, 430, . . . mμ. The interval between the wavelength settings need not be constant; indeed, the values selected will depend on the shape of the curve and the degree to which finer details of the curve must be secured. The values of % *T* found are plotted versus the wavelength values and a smooth curve is drawn through the points. Either by substitution in the formula $A = -\log T$ or by reading the absorbance scale provided additionally on most instruments, the corresponding absorbance values are obtained and plotted versus the wavelength values to obtain the absorbance curve. A typical transmittance curve and its equivalent absorbance curve are shown in Figure 36-2.

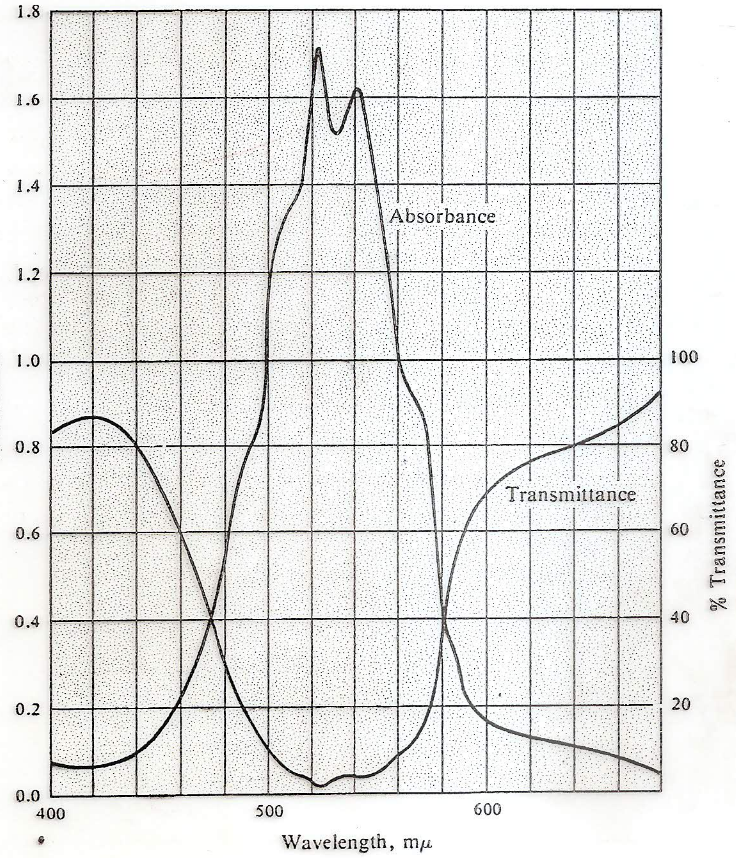
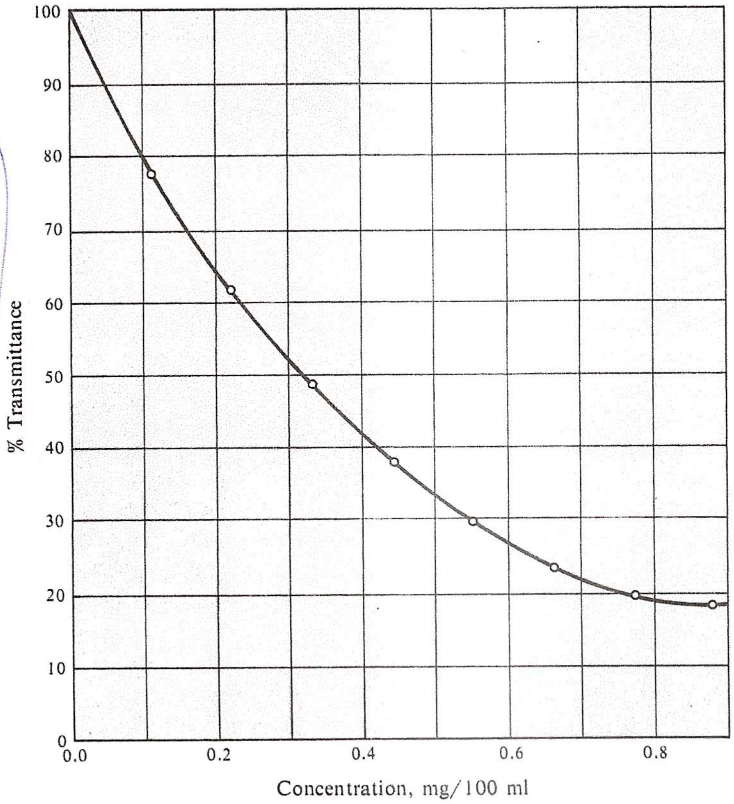


Figure 36-2. Absorbance and transmittance curves for $KMnO_4$ in water (40 mg/liter, 1-cm cell) for the region 400 to 680 mμ.

0,00025 M = 0,25 mM = 40 ppm sal = 14 ppm Mn

Plot of Transmittance versus Concentration

Since transmittance and concentration are related by a logarithmic function, a straight line is not obtained on plotting these two variables on ordinary (linear) graph paper (see Figure 36-3). This fact does not hinder the practical use of the



în logaritmica

Figure 36-3. Typical calibration curve, per cent transmittance versus concentration. (See also Figure 36-4.)

plot as a calibration curve, but it is difficult to decide from such a curve whether Lambert–Beer's law is obeyed and to judge whether the conditions for a photometric measurement

Plot of Absorbance versus Concentration

If Lambert–Beer's law is obeyed, a straight line is obtained on plotting either transmittance versus concentration on semilogarithmic graph paper or, what amounts to the same thing, absorbance versus concentration on linear graph paper. The latter method is usually preferred, because it is easier to interpolate on an equal-increment scale. For these two plots the slopes of the lines correspond to $-ab$ or $+ab$, respectively, in the expression of the law. Indeed the slope of the straight-line portion can be read and be used to calculate the concentration directly.

The absorbance versus concentration curve corresponding to the curve in Figure 36-3 is shown in Figure 36-4. Beer's law is

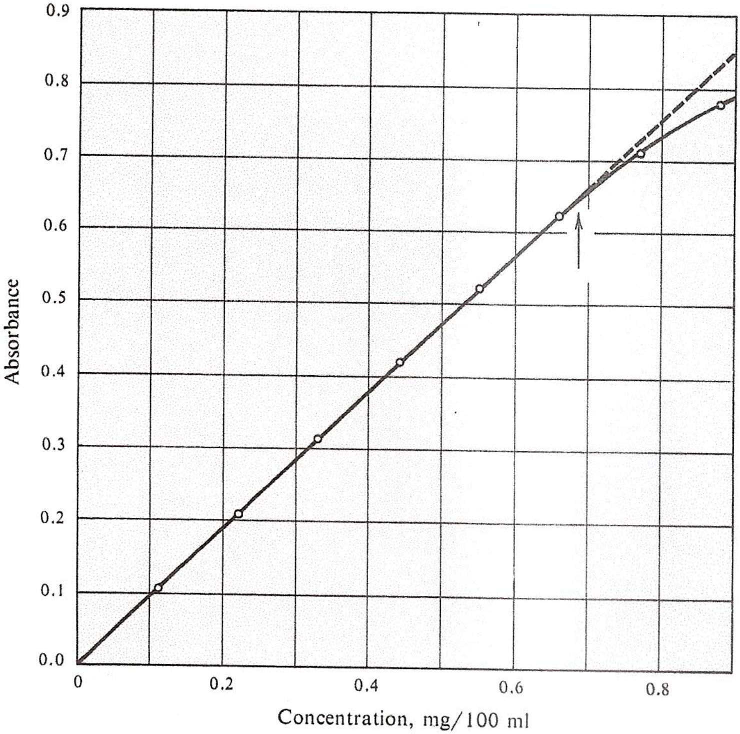


Figure 36-4. Typical calibration curve, absorbance versus concentration. Arrow indicates point at which deviation from Lambert–Beer's law becomes pronounced. (Same data as Figure 36-3.)

escala logarítmica

⇒ estica

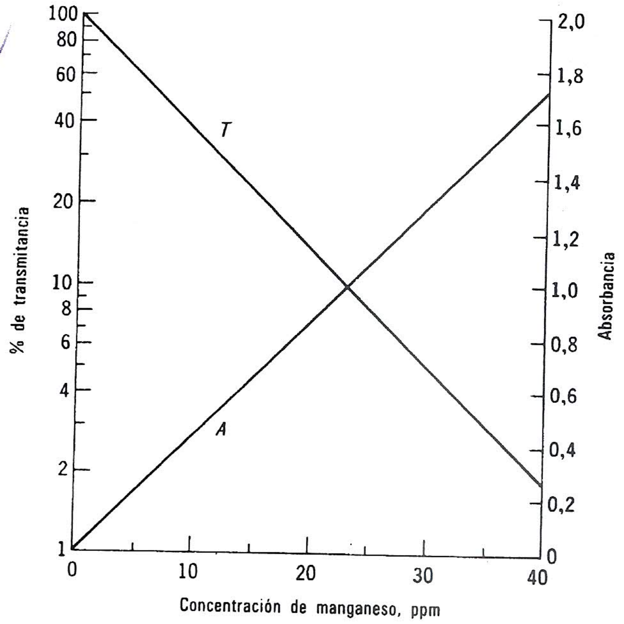


Fig. 31-11 Curvas patrón de disolución de permanganato, medidas a 526 mμ en células de 1,00 cm.

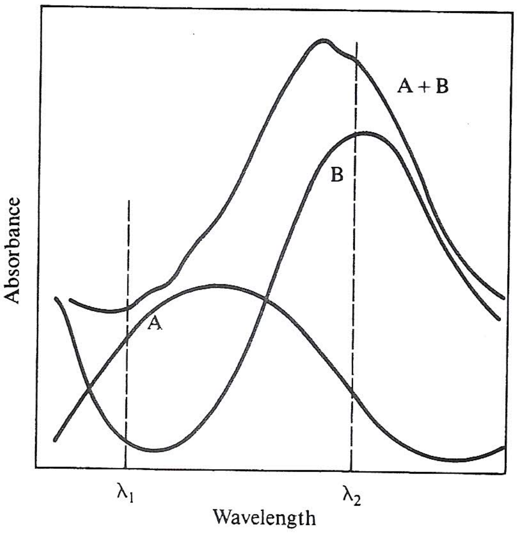


Figure 22–8
Absorption spectrum for a two-component mixture.

$$\frac{\sigma_c}{c} = \frac{0.434}{\log T} \times \frac{\sigma_T}{T}$$

Table 22–3
CATEGORIES OF INSTRUMENTAL INDETERMINATE ERRORS IN TRANSMITTANCE MEASUREMENTS

Category	Sources	Effect of T on Relative Standard Deviation of Concentration	
$\sigma_T = k_1$	Readout resolution; thermal detector noise; dark current and amplifier noise	$\frac{\sigma_c}{c} = \frac{0.434}{\log T} \times \frac{k_1}{T}$	(22–3)
$\sigma_T = k_2\sqrt{T^2 + T}$	Photon detector shot noise	$\frac{\sigma_c}{c} = \frac{0.434}{\log T} \times k_2 \sqrt{1 + \frac{1}{T}}$	(22–4)
$\sigma_T = k_3 T$	Cell positioning uncertainty; fluctuation in source intensity	$\frac{\sigma_c}{c} = \frac{0.434}{\log T} \times k_3$	(22–5)

Note: σ_T is the standard deviation of the transmittance measurements; σ_c/c is the relative standard deviation of the concentration measurements; T is transmittance; and k_1, k_2, and k_3 are constants for a given instrument.

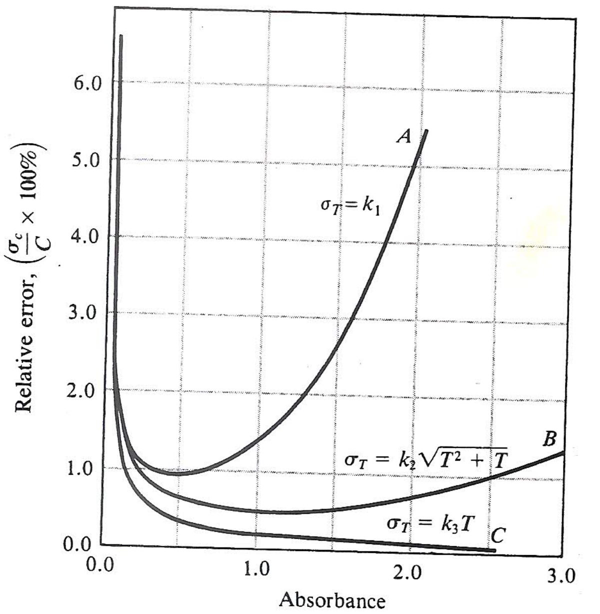


Figure 22–9
Error curves for various categories of instrumental uncertainties.

complex. The mathematical relationship can be obtained by differentiation of the expression of Lambert–Beer's law, but the derivation is beyond the scope of this textbook. Such a formula, however, was used to calculate the data leading to the curve shown in Figure 36-5. This plot allows the relative deviation in the concentration caused by an absolute photometric error of 1% T to be read. The curve has an interesting shape. It can be seen that the relative deviation in concentration is a minimum at a transmittance of about 37%. Here a photometric error of 1% T, that is, of 1 division on a 100-division transmittance scale, causes a relative deviation of 2.7% in the concentration. The same photometric error at 80% T produces a relative deviation of 5.6% in concentration. For a good instrument the actual photometric error encountered is often only 0.2% T, which at the optimum condition of 37% T yields a concentration value precise within 0.5%.

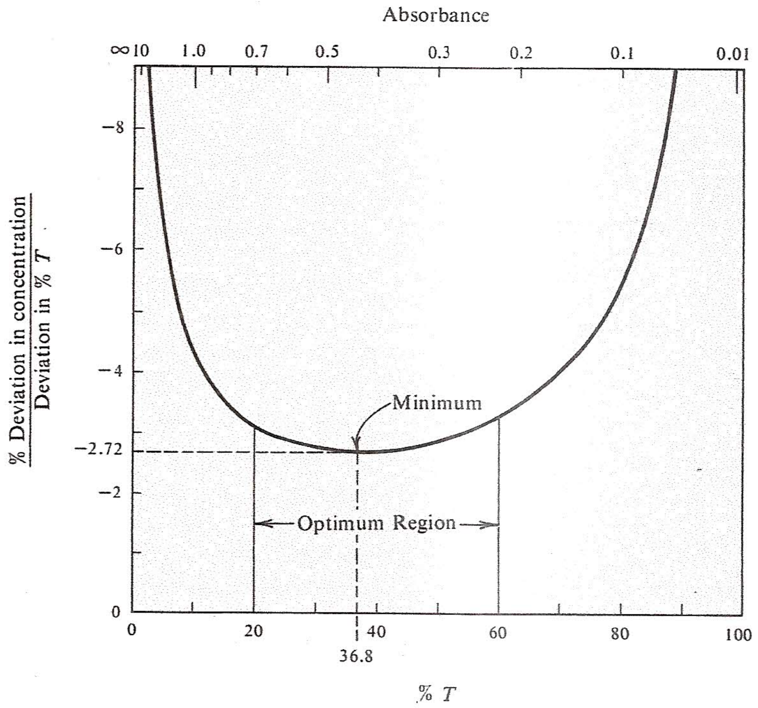


Figure 36-5. Plot of the relative deviation in concentration caused by a 1% photometric error versus per cent transmittance (lower abscissa scale) and absorbance (upper abscissa scale). Calculated from $100\ \Delta c/c\,\Delta T = 0.434/T \log T$, for $\Delta T = 1\%$.

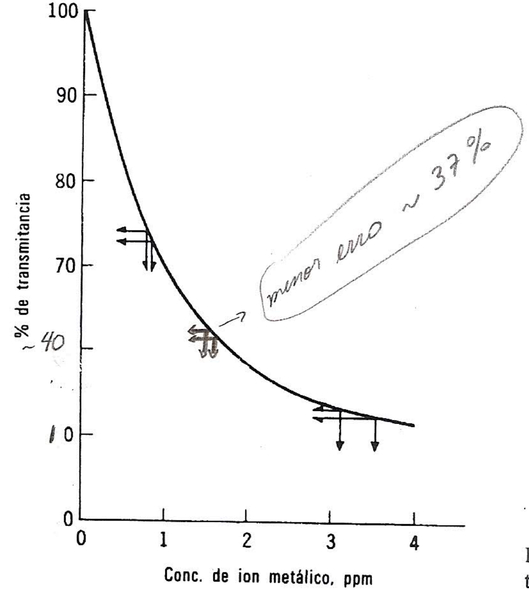
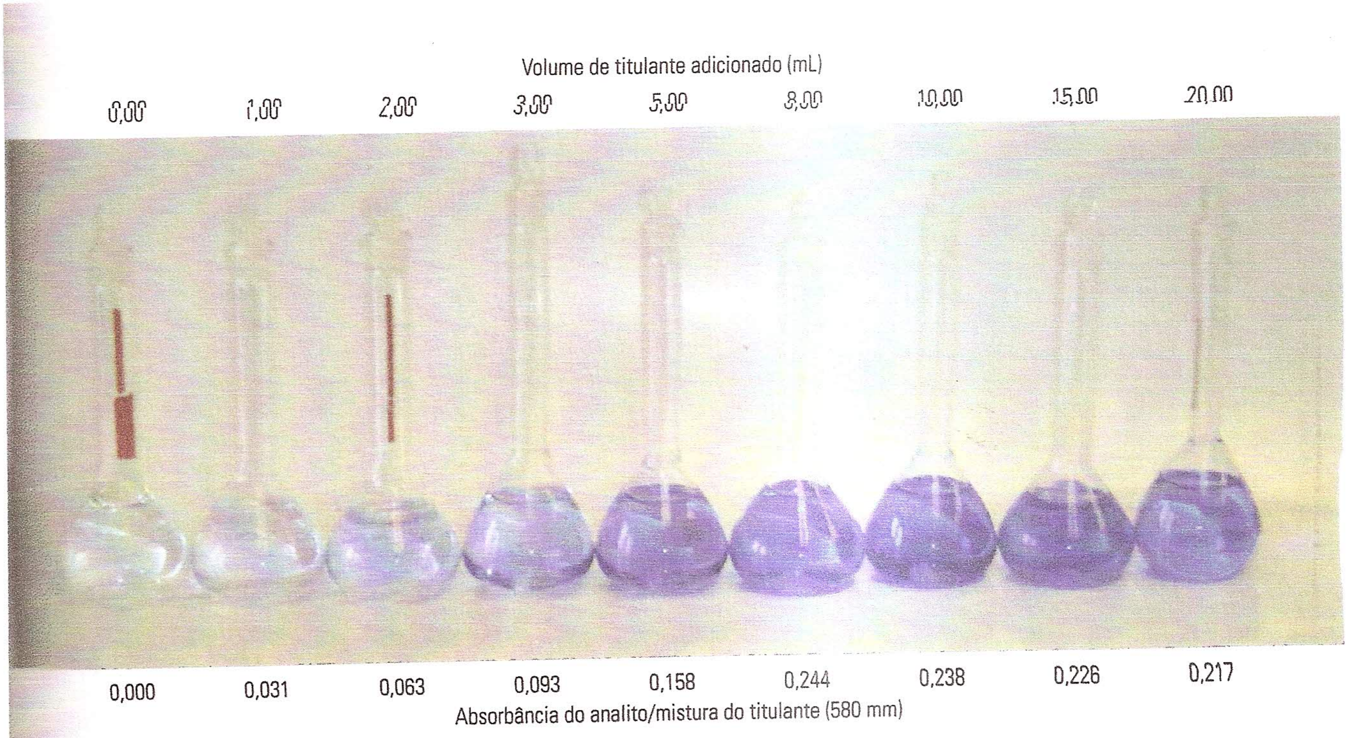


Fig. 31-10 Curva de calibración transmitancia-concentración.

Ayres



Exemplo de titulação espectrofotométrica, no qual uma amostra contendo uma quantidade fixa de Cu^{2+} é combinada com várias quantidades de trietilenotetramina (trien) como titulante para formar um complexo colorido. A concentração final de Cu^{2+} em cada balão volumétrico era de 1,43 × 10^{-3} *M*. Os volumes de titulante que foram adicionados a cada balão (antes de diluir o conteúdo com água até a marca) são fornecidos no topo da figura. As leituras de absorbância feitas das misturas analito/titulante resultantes são fornecidas na parte inferior. Com base nesses dados, foi determinado que o ponto final da titulação ocorreu quando o equivalente a 7,73 mL de trien foi adicionado a um dos balões (ver o Capítulo 18 para mais detalhes sobre esse método).

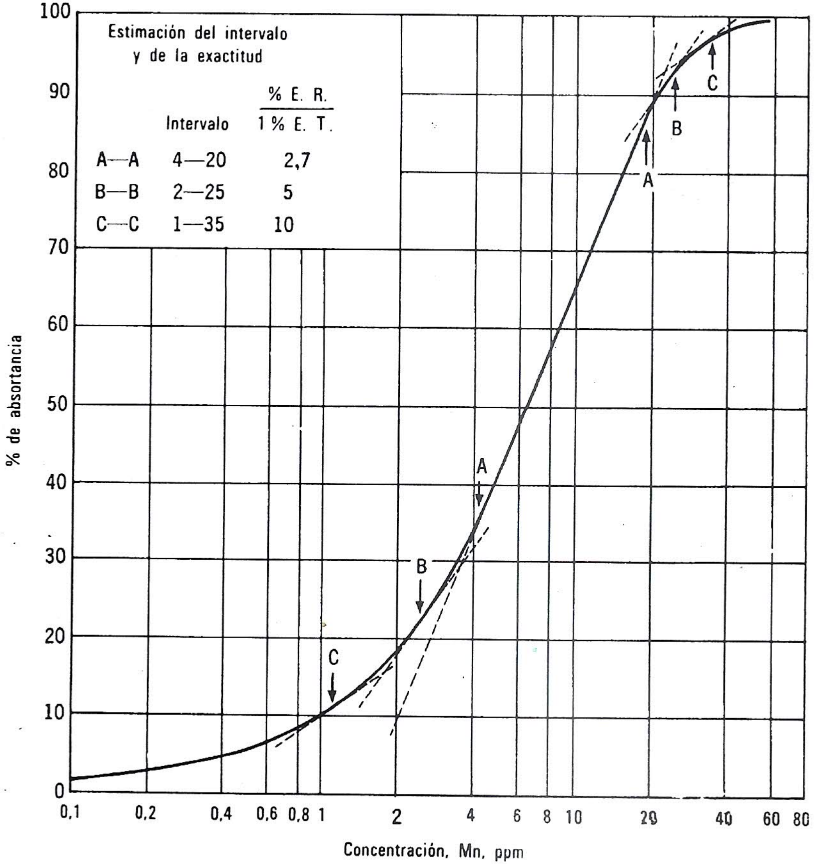


Fig. 31-15 Representación de Ringbom para disoluciones de permanganato medidas a 526 mμ en células de 1,00 cm.

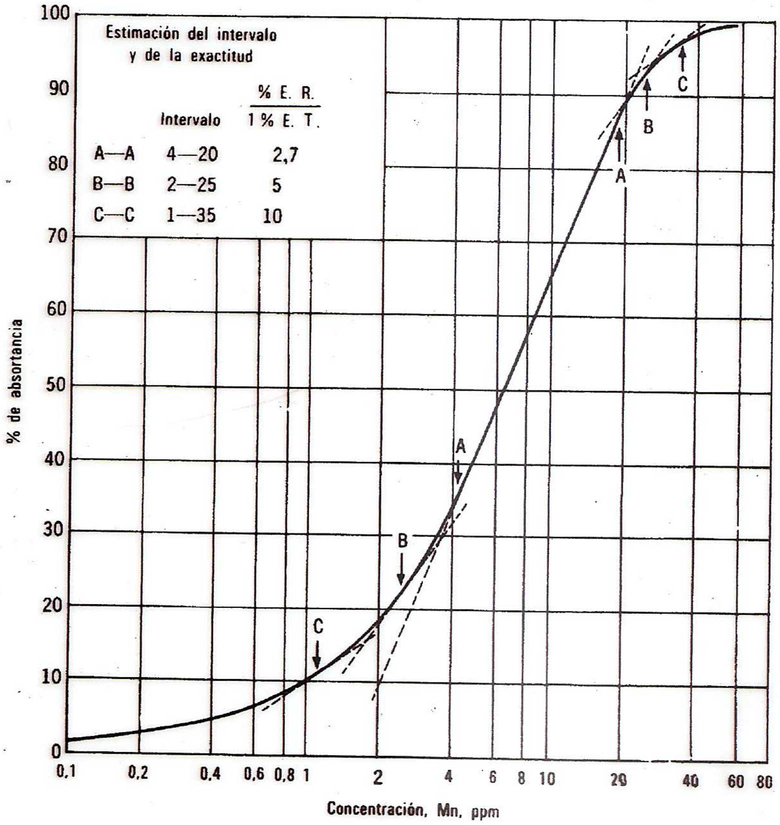


Fig. 31-15 Representación de Ringbom para disoluciones de permanganato medidas a 526 mμ en células de 1,00 cm.

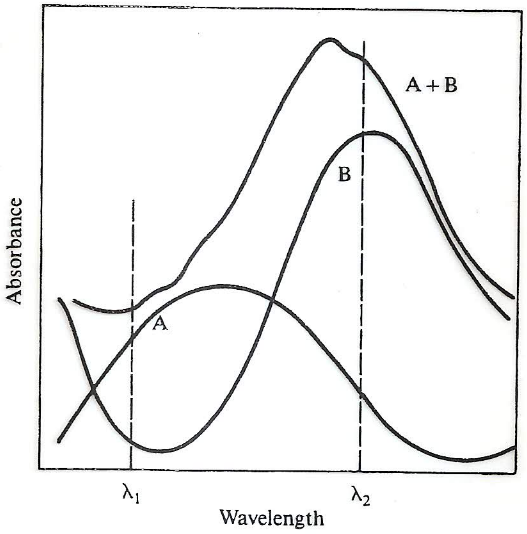


Figure 22–8

Absorption spectrum for a two-component mixture.

$$\frac{\sigma_c}{c} = \frac{0.434}{\log T} \times \frac{\sigma_T}{T}$$

Table 22–3

CATEGORIES OF INSTRUMENTAL INDETERMINATE ERRORS IN TRANSMITTANCE MEASUREMENTS

Category	Sources	Effect of *T* on Relative Standard Deviation of Concentration
$\sigma_T = k_1$	Readout resolution; thermal detector noise; dark current and amplifier noise	$\frac{\sigma_c}{c} = \frac{0.434}{\log T} \times \frac{k_1}{T}$ (22–3)
$\sigma_T = k_2\sqrt{T^2 + T}$	Photon detector shot noise	$\frac{\sigma_c}{c} = \frac{0.434}{\log T} \times k_2 \sqrt{1 + \frac{1}{T}}$ (22–4)
$\sigma_T = k_3 T$	Cell positioning uncertainty; fluctuation in source intensity	$\frac{\sigma_c}{c} = \frac{0.434}{\log T} \times k_3$ (22–5)

Note: σ_T is the standard deviation of the transmittance measurements; σ_c/c is the relative standard deviation of the concentration measurements; T is transmittance; and k_1, k_2, and k_3 are constants for a given instrument.

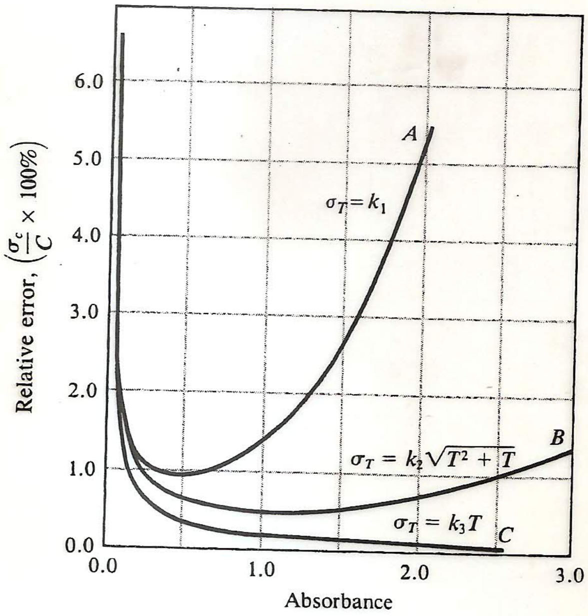


Figure 22–9

Error curves for various categories of instrumental uncertainties.

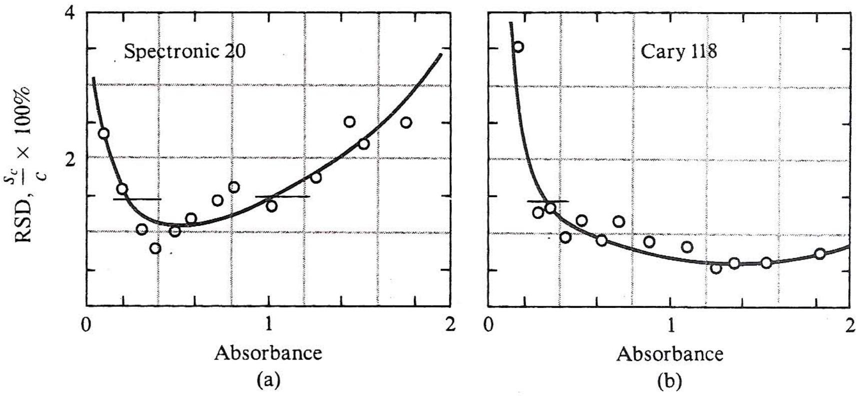
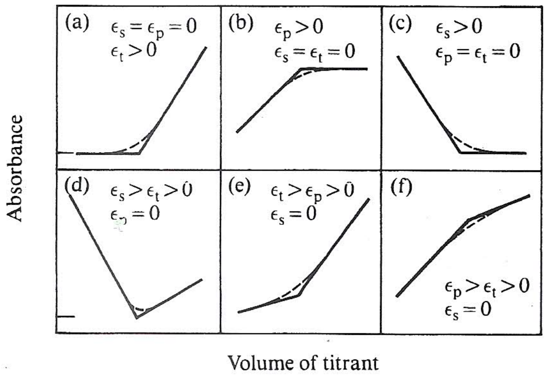


Figure 22–10

Experimental curves relating relative concentration uncertainties to absorbance for two spectrophotometers. Data obtained with (a) a Spectronic 20, a low-cost instrument (Figure 22–2), and (b) a Cary 118, a research-quality instrument. (From W. E. Harris and B. Kratochvil, *An Introduction to Chemical Analysis,* p. 384. Philadelphia: Saunders College Publishing, 1981. With permission.)

Figure 22–11

Typical photometric titration curves. Molar absorptivities of the substance titrated, the product, and the titrant are ε_s, ε_p, ε_t.



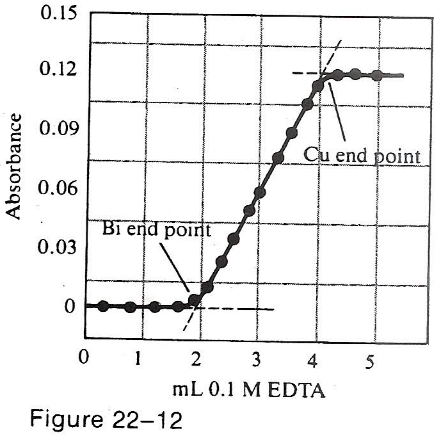


Figure 22–12

Photometric titration curve at 745 nm for 100 mL of a solution that was 2.0×10^{-3} M in Bi^{3+} and Cu^{2+}. (A. L. Underwood, *Anal. Chem.*, **1954,** *26,* 1322. With permission of the American Chemical Society.)

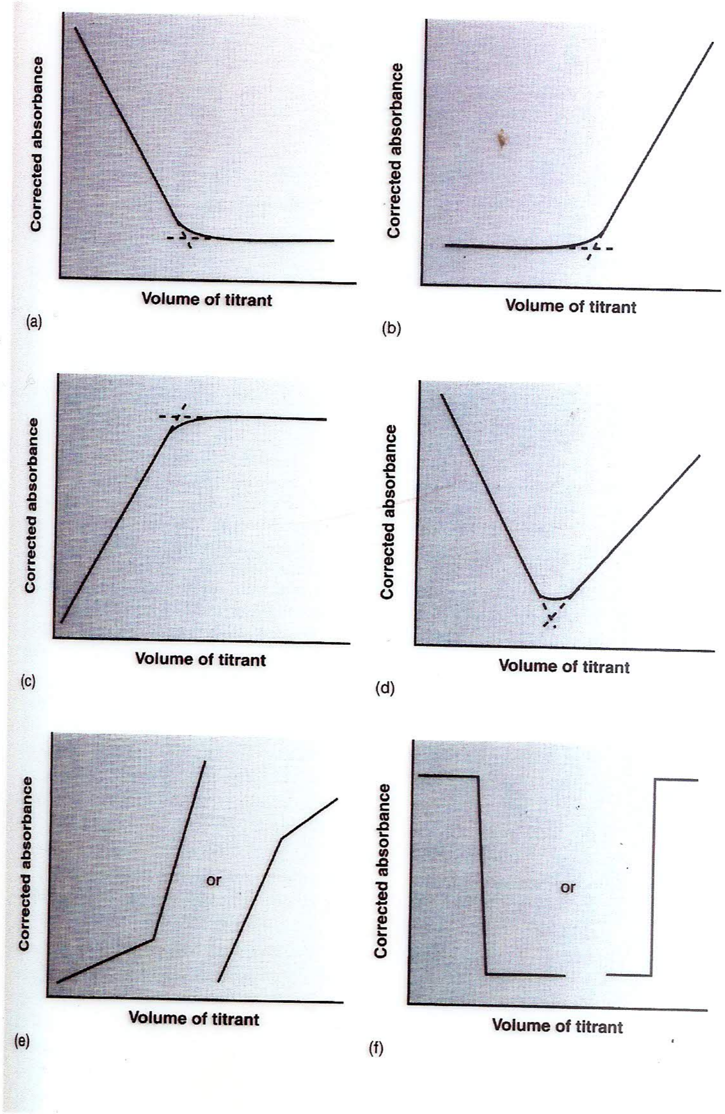


Figure 9.30

Spectrophotometric titration curves for the titration of an analyte, A, with a titrant, T, to form a product, P, in the presence of a visual indicator. Titration curves are shown for cases where (a) only A absorbs; (b) only T absorbs; (c) only P absorbs; (d) A and T absorb; (e) P and T absorb; and (f) only the visual indicator absorbs.