8 - Spectrophotometry


1] The detection limit of any instrumental method is best expressed as which of the labeled points in the graph above? ${ }^{1}$

2] Which of the labeled features in the curve above best represents the nonlinear region? ${ }^{2}$
3] Which of the labeled features in the curve above best represents the linear range? ${ }^{3}$
4] Which of the labeled features in the curve above best represents the background? ${ }^{4}$
5] What best describes the reason for using the method standard addition over the calibration curve? ${ }^{5}$

6] The method of least squares fits a line (L) to a set of $x, y$ data by $\qquad$ ${ }^{6}$

7] When can Beer's law fail? ${ }^{7}$
8] Sensitivity in a Beer's law analysis can be best described as $\qquad$ 8

9] Consider the following calibration curve:
The sensitivity is represented by: $\qquad$ 9

The detection limit is represented by $\qquad$


10] A sample solution gave a signal of 0.112 absorbance units at 553 nm . When 0.120 mM of standardized analyte was introduced into the sample it gave a signal of 1.98 . What is the concentration of that analyte? ${ }^{10}$

11] A sample solution of an analyte has an absorbance of 0.229 . A solution of standard has an absorbance of 0.327 when that analyte has a concentration of $3.44 \mathrm{e}-3 \mathrm{M}$. Assuming that Beer's law applies to both solutions what is the concentration of analyte in the sample? Also assume that the absorbance of the blank solution is zero. ${ }^{11}$

12] The absorbance of a solution that is 153 ppm in a metal ion is 0.55 at a wavelength of 330 nm . A sample solution of that same metal ion is measured at the same wavelength and is 0.37 . What is the concentration of that metal ion in the sample? ${ }^{12}$

13] A sample solution with an unknown concentration of herbicide ( $\lambda_{\max }=636 \mathrm{~nm}$ ) was analyzed by absorption spectroscopy. A 10.0 mL sample was diluted to 500.0 mL and the absorbance was measured as 0.366 . Another 10.0 mL sample was mixed with 10.0 mL of $5.00 \times 10^{-3} \mathrm{M}$ then diluted to 500.0 mL . The absorbance of this solution was measured as 0.559 . The absorbance of the blank was zero. What is the concentration of this herbicide? ${ }^{13}$

14] A sample solution was analyzed by the standard addition method using its absorbance at 455 nm .
a) In the first experiment a $10.00-\mathrm{mL}$ of aqueous sample was diluted to $500.0-\mathrm{mL}$ with water. Its measured absorbance is 0.378 .
b) In the second experiment $10.00-\mathrm{mL}$ was mixed with $1.00-\mu \mathrm{L}$ of $3.22 \mathrm{e}-5 \mathrm{M}$ and diluted to $500.0-\mathrm{mL}$ with water. The measured absorbance of this solution is 0.402 . What is the concentration of the analyte in the sample? ${ }^{14}$

15] A sample was measure for a particular herbicide $\left(\lambda_{\max }=311 \mathrm{~nm}\right)$ by UV-vis absorbance spectroscopy.
a) In the first experiment a 15.0 mL aliquot of the sample was dissolved in 500.0 mL of water. An absorbance measurement of 2.50 mL of the diluted sample was taken at 311 nm and yielded 0.344 abs .
b) In a second experiment a 15.0 mL aliquot of the sample was dissolved in 500.0 mL of water then 10.0 mL of $8.44 \times 10^{-3} \mathrm{M}$ of that herbicide was added. An absorbance measurement of 2.50 mL of this solution taken at 311 nm and yielded 0.544 abs.
c) Finally, the absorbance of water was measured at 311 nm and found to be 0.017 .

What is the molar concentration of this herbicide in the sample? ${ }^{15}$
16] A visible absorption analysis was conducted on a red dye ( $\lambda_{\max }=566 \mathrm{~nm}$ ). A 1.00 mM standard solution of that dye yields an absorption of 0.455 . The absorption in 0.00 mM of that dye is 0.00 . An unknown solution of that dye gives an absorption of 0.522 . What is the concentration of that red dye in the unknown? ${ }^{16}$

17] A solution of $\mathrm{Pb}^{2+}$ analysis in drinking water was conducted by UV absorbance spectroscopy. In the first run a sample of $\mathrm{Pb}^{2+}$ gave an absorbance of 0.400 . In a second run that sample had the concentration of $\mathrm{Pb}^{2+}$ increased by 1.00 ppm and its measured absorbance is now 0.700 . What is the concentration of $\mathrm{Pb}^{2+}$ in the sample? ${ }^{17}$

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## Answers

${ }^{1} \mathrm{E}$
${ }^{2} \mathrm{C}$
${ }^{3} \mathrm{~B}$
${ }^{4} D$
${ }^{5}$ To accommodate the effects of a complex matrix
${ }^{6}$ minimizing $\Sigma\left(y_{i}-y_{L}\right)^{2}$
${ }^{7}$ when $\mathrm{A}>1$ also $\mathrm{S} / \mathrm{b}<3$
${ }^{8}$ The product of $\mathrm{e} \times \mathrm{b}$ in Beer's Law: $\mathrm{A}=\mathrm{ebc}$
${ }^{9} \mathrm{M}$ and $\mathrm{a}^{\prime}$
${ }^{10} y=m x+b$ or $S=m c+b, b=0.112$ and $m=(0.198-0.112) / 0.120=0.717$
$S=0.717 c+0.112$, method of standard addition, find $x$-int
$0=0.717 \mathrm{c}+0.112, \mathrm{c}=0.156 \mathrm{mM}$
${ }^{11} 0.229 / 0.327=c / 3.44 e-3$
${ }^{12} A=e b c ;$ must find eb for the system.

$$
\begin{aligned}
& 0.55=\mathrm{eb} * 153 \mathrm{ppm} \\
& \mathrm{eb}=3.5 \underline{9} \mathrm{e}-3 \\
& 0.37=3.5 \underline{9} \mathrm{e}-3^{*} \mathrm{c} \\
& \mathrm{c}=103 \mathrm{ppm}
\end{aligned}
$$

13
$0.559=k C_{x}(10.0 / 500.0)+k 5.00 e-3^{*}(10.00 / 500.0)$
$-0.366=-k C_{x}(10.0 / 500.0)$
$0.193=k 5.00 e-3^{*}(10.00 / 500.0)$

$$
\begin{aligned}
& k=1930 \text { use } 0.559=k C_{x}(10.0 / 500.0) \\
& 0.559=1930 C_{x}(10.0 / 500.0)
\end{aligned}
$$

$C_{x}=9.48 \mathrm{e}-3 \mathrm{M}$
${ }^{14}$ Part a

$$
0.378=k(10.00 / 500.0) \mathrm{c} \backslash
$$

Part b

$$
\begin{aligned}
& 0.402=k(10.00 / 500.0) c+k(1.00 \mathrm{e}-6 / 0.5000) 3.22 \mathrm{e}-5 \\
& 0.402=0.378+k(1.00 \mathrm{e}-6 / 0.5000) 3.22 \mathrm{e}-5 \\
& k=3.7 \underline{3} \mathrm{e} 8 \\
& 0.378=3.7 \underline{3} \mathrm{e} 8(10.00 / 500.0) \mathrm{c}
\end{aligned}
$$

$c=5.1 \mathrm{e}-8 \mathrm{M}$
${ }_{15} A_{1}=\frac{15.0}{515.0} k c \quad$ Solve for $k \quad k=\frac{11.2}{c}$
$A_{2}=\frac{15.0}{525.0} k c+\frac{10.0}{525.0} k \times 8.44 \times 10^{-3} \quad 0.544-0.017=0.0286 k c+1.608 \times 10^{-4} k$
Sub \#1 into above $\quad 0.527=0.0286 \frac{11.2}{c} c+1.608 \times 10^{-4} \frac{11.2}{c}$
$0.527=0.320+\frac{1.80 \times 10^{-3}}{c}$
Solve for $\mathrm{c} \quad \mathrm{c}=8.70 \mathrm{e}-3 \mathrm{M}$
${ }^{16} \mathrm{~A}=\mathrm{ebc} \quad 0.455=\mathrm{eb}(1.00 \mathrm{mM}) \quad \mathrm{eb}=0.455 \quad \mathrm{Au}=0.522=0.455^{*} \mathrm{c} \quad \mathrm{c}=1.15 \mathrm{mM}$
${ }^{17}$ The slope of the standard addition curve is $0.700-0.400 / 1.000 \mathrm{ppm}=0.300$

$$
\begin{array}{lll}
\text { Line is } & y=0.300 x+0.400 & \text { find } x \text {-int } \\
& 0=0.300 x+0.400 & x=-1.33 p p m
\end{array}
$$

Using graph:


