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A STUDY OF ABSORPTION SPECTRUM

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Abstract:

Part I: Beer-Lambert law

To record absorption spectrum of potassium dichromate solution and determine molar extinction coefficient of potassium dichromate.

Part II: Absorption spectrum

To determine oscillator strength and life time for electronic transition in potassium dichromate.

Absorption and absorption spectrum

Absorption of radiation: Beer's Law

Consider a narrow beam of monochromatic light of wave length λ and of intensity $I_o(\lambda)$ incident on a column of liquid- a solution- held in a transparent glass cell as shown in Figure 6.1. The beam suffers attenuation while traversing a length L of the solution and the transmitted intensity $I_t(\lambda)$ is less than the incident intensity. The possible mechanisms for the attenuation of incident beam are: (a) reflection at air-glass interface, (b) absorption by glass, (c) reflection at glass-solution interface, (d) absorption by solute, (e) absorption by solvent, (f) scattering by solution and (g) refraction by the cell and solution. The attenuation depends on the wavelength of the radiation and nature of the atom / molecule, the path length and temperature of the medium. There is an exponential relation between incident intensity $I_o(\lambda)$ and the intensity $I_t(\lambda)$ of the beam which emerges from a plane parallel layer of the absorbing solution of thickness L and concentration C and is known as Beer's law:

$$I_t(\lambda) = I_o e^{-\varepsilon'(\lambda)CL} \qquad (6.1)$$

where the absorption coefficient $\varepsilon'(\lambda)$ is a constant characteristic of the absorber.

In a measurement of $I_o(\lambda)$ and $I_t(\lambda)$ with a narrow beam of monochromatic radiation, following terms are defined for the absorbing medium.

1. Transmittance $T(\lambda)$

$$T(\lambda) = \frac{I_t(\lambda)}{I_o(\lambda)} \qquad (6.2)$$

In practice, percentage transmittance is often used,

$$\%T(\lambda) = \frac{I_t(\lambda)}{I_o(\lambda)} x100 \qquad (6.3)$$

2. Absorbance $A(\lambda)$

$$A(\lambda) = -\log_{10} T(\lambda) = \log_{10} \frac{I_t(\lambda)}{I_o(\lambda)} \qquad (6.4)$$

3. Absorptivity or λ extinction coefficient $a(\lambda)$

From Beer's law,

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$$ln\frac{I_t(\lambda)}{I_o(\lambda)} = \varepsilon'(\lambda)CL \qquad (6.5)$$

So $A(\lambda)$ can be expressed in terms of absorber parameters,

$$A(\lambda) = \frac{1}{2.303} ln\frac{I_t(\lambda)}{I_o(\lambda)} = \frac{1}{2.303}\varepsilon'(\lambda)CL = a(\lambda)CL \qquad (6.6)$$

From Equation 6.6 it is seen that for monochromatic radiation, absorbance $A(\lambda)$ is directly proportional to the path length L through the medium and the concentration C of the absorbing species. The magnitude and dimensions of absorptivity (or extinction coefficient) $a(\lambda)$ will clearly depend upon the units used for L *and* C. If the path length L is expressed in centimeters and C is expressed in g/l then the absorptivity is in $lg^{-1}\ cm^{-1}$

.

Beer-Lambert law, Molar extinction coefficient

If C is expressed in moles per liter and L in centimeter then absorptivity a(λ) is called molar absorptivity or molar extinction coefficient ε(λ) and then Equation (6.6) becomes the Beer-Lambert law:

$A(\lambda) = \varepsilon(\lambda)CL \qquad (6.7)$

The molar extinction coefficient $\varepsilon(\lambda)$ has the unit liter.mol^{-1}.cm^{-1}. It is an intrinsic property of the absorbing material that measures its ability to absorb radiation and varies with wavelength of the radiation in a manner characteristic to the material. Its value depends slightly on the solvent used and on the temperature of the solution but not on the concentration. It is a good parameter to compare quantitatively the absorption of various substances. From Equation 6.7 we see that a plot of $A(\lambda)$ versus C is a straight line with slope equal to $\varepsilon(\lambda)$ and can be used to obtain $\varepsilon(\lambda)$.

Limitations to Beer's Law and its application

1. At high concentration (usually C> 0.001 mol), the average distance between the absorbing species is diminished to the point where each affects the charge distribution of its neighbors. This interaction, in turn can alter their ability to absorb a given wavelength of light. Because the extent of interaction depends on the concentration, at high concentration the linear relation between the absorbance and the concentration is affected. A similar effect is observed when electrolytes are present in the solution whose concentration is more than the concentration of absorbing species. Some exceptions are encountered when the molecular interactions is ordinarily not significant at concentrations less than 0.01 mol in some organic ions or molecules.

2. For best results, the absorbance should be kept in the range 0.2 -1. If the absorbance is 2, then only 1% of radiation initially present reaches the detector. This not only means the sensitivity of the detector should be high, but that any scattered light present becomes a more important fraction of the radiation reaching the detector. By choosing a slit of very small width this effect can be minimized.

3. Deviations from Beer's law also arises because dependence of ε(λ) upon the refractive index of the medium. This correction is never significant for the concentration less than 0.01 mol/liter.
4. Apparent deviations are observed when absorbing species associates or dissociate, or react with the solvent to generate a product which has a different absorbing spectrum than that of absorbing species.
5. Beer's law is strictly applicable for monochromatic light but when poly chromatic light is used, the variation of ε(λ) with wavelength causes deviation in the linear relation of absorbance with the concentration of the absorbing species.

Absorption spectrum

The absorbing characteristics of a species are conveniently described by means of an absorption spectrum, which is a plot of some function of the attenuation of a beam of radiation, such as A(λ), versus wavelength (λ) or frequency (ν) or wave number ($\bar{\upsilon}$). Molecular absorption spectroscopy based upon ultraviolet, visible, and infrared radiation is widely used for the identification and determination of numerous inorganic, organic and biochemical species. It is employed primarily for quantitative analysis and is probably more extensively used in chemical and clinical laboratories throughout the world than any other single method. The spectral data such as position of peaks and its/their absorbance can serve as rough guide for the identification purposes. Both the position of the peak and its absorbance are influenced by solvent effects as well as by structural details of the molecule. A change in pH value of the medium generally has a profound effect upon the absorption spectrum of a molecule containing hetero atoms

Oscillator strength

The strength of an electronic transition is expressed in terms of oscillator strength *f*. It is defined as the ratio of the experimental transition probability to that of the ideal case of a harmonic oscillator. Classically, it measures the effective number of electrons whose oscillations give rise to particular absorption or emission band and is a dimensionless quantity. It is related to the extinction coefficient over the integral of the absorption band on wave number scale:

$$f = 4.33X10^{-9} \int_{min}^{max} \varepsilon(\bar{\upsilon}) d\bar{\upsilon} \qquad (6.8)$$

where the min and max limits on the integration refer to respective minimum and maximum limits of the absorption band. In practice, the integral in Equation 6.8 is evaluated as area under the curve in a plot of ε(λ) wave number ($\bar{\upsilon}$) .

Lifetime

Life time τ of an excited singlet state is an important parameter that can be approximately determined from the absorption spectra to that from the fluorescent decay since

the probability of the downward transition accompanied by fluorescence is proportional to that of the corresponding upward transition (absorption). The natural radiative lifetime of the atom or a molecule is the time spent by the electronically excited electron in the higher energy states of an atom or a molecule if left unperturbed by the environment. In the system of large number of particles, the rate of decay follows a first order rate flow and can be expressed in terms of the rate of emission of radiation due to decay as,

$I(t)=I(0)e^{-K_R t}$ (6.9)

where $I(0)$ and $I(t)$ are the intensity of emitted radiation at zero time and at any time t after the exciting radiation is cut off and K_R is the rate constant for the emission process with dimension of reciprocal of time. If $K_R=1/\tau$ then

$I(t)=1(0)/e$ (6.10)

Hence, the lifetime is defined as the time over which the radiation intensity falls to 1/e times of its initial value. This is called the natural radiative lifetime τ_N.

The lifetime of an electronic level will be intrinsic radiative life time if there are no other modes of decay. The radiative lifetime can be calculated by taking the integration over the absorption band on wave number scale:

$$\tau_N = \frac{3.47X10^8}{\bar{v}^2 \int_{min}^{max} \varepsilon(\bar{v})d\bar{v}} \quad (6.11)$$

where $\bar{v}_m$ is the absorption maximum and the integration is carried out over the whole absorption spectrum.

Using Equations 6.10 and 6.11 we get a relation between radiative life τ_N radiative life time and oscillator strength f:

$$\tau_N = \frac{1.503}{\bar{v}^2 f} \quad (6.12)$$

Absorption in potassium dichromate

Potassium dichromate solution in water is widely used as an absorption standard. Therefore we used this solution to study the Beer-Lambert law and to determine the oscillator strength and life time for its transitions in the visible region. Its standard absorption spectrum is given in Figure 6.3. It shows two absorption bands with peak absorbance at 257 nm and 350 nm.

Recording absorption spectrum using FOS

To record an absorption spectrum using FOS it is set up as shown Figure 6.2. In this experiment an external light source with continuous spectrum is used. The sample solution is taken in a standard 1 cm quartz cuvette. The cell has 1 cm sides and is 4 cm tall and provided 1 cm path length to the optical beam normally incident on it. The cell can is held vertically in a sample holder rigidly mounted on a flat optical base plate and can be tightly covered to totally avoid stray light falling on it. The first optical fibre which is connected between the light source

and the sample holder is the illumination fibre. It transmits the light from the source on to the sample cuvette normally. The second optical fibre which is connected between the sample holder and the PC2000 spectrometer is the read fibre. It carries the light transmitted through the sample to spectrometer. First the absorption spectrum of the solvent is recorded. This is referred to as 'Reference'. Next the absorption spectrum of the 'sample'- solution in this case- is recorded. When the 'processed' spectrum of the 'sample' is saved the absorption spectrum of the solvent is subtracted from the absorption spectrum of the solution and the absorption spectrum of the solute is saved as a file. This is the desired absorption spectrum.

Experimental

Potassium dichromate solution

Commercially available, 99.8% pure laboratory reagent grade potassium dichromate and 99.9% pure sulphuric acid and doubly distilled water are used to prepare potassium dichromate solution in acidic medium. First a stock solution S1 with highest concentration of 0.002126 mole/liter is prepared by dissolving 0.00125 g of potassium dichromate in 2 ml water. Next, 1 ml of this stock solution S1 is taken and 1 ml of water is added to get the second solution S2 with 0.001063 mole/liter concentration. Starting with 1 ml of S2 and adding 1 ml of water third solution S3 with 0.000531 mole/liter concentration prepared. The procedure is repeated to get solutions S4, S5, S6, S7 and S8 with concentrations of 0.000266, 0.000133, 0.0000664, 0.0000332 and 0.0000166 mole/liter. For recording absorption spectra, 2ml solution of desired concentration is taken in the standard 1 cm cuvette of 4 ml capacity.

Beer's law

The PC2000 FOS is set up to record absorption spectrum as shown in Figure 6.2. The operating software OOIBase32 is launched. The calibration coefficients provided by the manufacturer are used and the spectrometer is configured. Dark spectrum is 'stored' and 'subtracted' and the 'Scope Mode' of the spectrometer is activated. The cuvette with distilled water is positioned in to sample holder and covered. 'Reference' spectrum is 'saved'. Now 'Absorbance Mode', 'Transmittance Mode' and 'Irradiance Mode' of the spectrometer also become active. The 'Absorbance Mode' is selected and 'Snapshot' of the absorption spectrum is taken. The 'Processed' spectrum is saved as the absorption spectrum of the solvent, the 'Reference' spectrum. Next 2 ml solution of potassium dichromate of desired concentration is taken in the cuvette and is placed in the sample holder and covered. With 'Absorbance mode' the absorption spectrum is viewed. If the concentration is proper, an absorption spectrum with two bands will be seen on the PC monitor as shown in Figure 6.4. If the concentration is high and absorbance is greater than 1.6 a broad plateau may is seen indicating violation of limitations of Beer's law. So a sample with lower concentration that clearly shows two broad peaks as in Figure 6.4 is chosen and 'Snapshot' of the absorption spectrum is taken. The 'Processed' spectrum is saved as the absorption spectrum of the solution at that concentration, the 'Sample' spectrum. The procedure is repeated to record the absorption spectrum of other samples with lower concentrations.

The recorded spectrum consisting of the two absorption bands is scanned at intervals of about 5 nm from the beginning to the end: Cursor is positioned successively at 16 points between 247.17 nm to 315.15 nm on the 257 nm band and at 14 points between 321.51 nm to 384.62 nm on the 257 nm band and the corresponding wavelength Î» (listed in Table 6.1) and absorbance A(2) are noted. The procedure is repeated for the absorption spectrum of each of the samples.

Data

Standard data

1. Figure 6.3 is the standard absorbance spectrum for potassium dichromate in acidic (0.005M sulphuric acid) medium.

Experimental data

1. Figure 6.4 shows a photograph of the PC monitor with absorption spectrum for 0.000266 mole/liter concentration solution (S4). The absorption spectrum shows two broad peaks. The figure also shows the solution in a tube which is held in front of the monitor while taking the shot.
2. Figures 6.5 to 6.10 show absorption spectra for potassium dichromate solution with the respective concentration indicated.
3. Figure 6.11 shows absorption spectra for potassium dichromate solution with six different concentrations overlayed in a single graph.

Calculations, results

Absorption spectrum

The absorption spectrum for potassium dichromate has two broad bands. The first band has maximum at 350 nm for all the concentrations in agreement with standard spectrum (Figure 6.2). The second band has maximum between 257 nm and 280 nm depending on the concentration. Thus the maximum agrees with standard value of 257 nm only at low concentration and its red shift with concentration may be due to some reactions. Figure 6.11 shows dramatically that absorbance increases with concentration and that with increasing concentration possibilities of reactions leading to red shift of the absorbance peak. The two peaks are treated as two independent absorption spectra and are referred to as 257nm peak and 350nm peak hereafter.

Beer-Lambert law, Molar extinction coefficient

Then Beer-Lambert law (Equation 6.7) linear plot of A(λ) versus C for the 16 values of λ for 257nm band and for the 14 values of λ for 350nm band are obtained by linear regression to get the values of ε(λ) at the these λ. A typical linear plot at 295.14 nm for the 280nm band and at λ = 370.37 nm for the 350nm band are shown in Figures 6.12 and 6.13 respectively. The values of molar extinction coefficient ε(λ) at 16 values of λ for 257nm band and for the 14 values of λ for 350nm band are obtained from the above linear plots are given in Table 6.1.

Oscillator strength, Lifetime

Using the data in Table 6.1 molar extinction coefficients versus wave number plots obtained for 257 nm band and for 350 nm band are shown in Figure 6.14 and 6.15 respectively.

Using the value of the area under the curves in these Figures 6.14 and 6.15 in to Equation 6.8 the oscillator strength are obtained.

1. 257 nm band: $f = 4.33X10^{-9}\int_{min}^{max}\varepsilon(\bar{v})d\bar{v} = 4.33X10^{-9}X1.4924X10^{9} = 6.462$
2. 350 nm band: $f = 4.33X10^{-9}\int_{min}^{max}\varepsilon(\bar{v})d\bar{v} = 4.33X10^{-9}X1.09113X10^{9} = 4.725$

Using the value of the area under the curves in these Figures 6.14 and 6.15 in to Equation 6.11 the life time are obtained.

1. 257 nm band:

$$\tau_N = \frac{3.47X10^{8}}{\bar{v}_m^2\int_{min}^{max}\varepsilon(\bar{v})d\bar{v}} = \frac{3.47X10^{8}}{(3.142x10^{6})^2X1.4924X10^{9}} = 1.83X10^{-14}s$$

2. 350 nm band:

$$\tau_N = \frac{3.47X10^{8}}{\bar{v}_m^2\int_{min}^{max}\varepsilon(\bar{v})d\bar{v}} = \frac{3.47X10^{8}}{(2.9x10^{6})^2X1.09113X10^{9}} = 3.78X10^{-14}s$$

These results are presented in Table 6.2.

Table 6.1 Molar extinction confident ε(λ) for selected wavelength λ under the two bands in the absorption spectrum of potassium dichromate solution.

SN	257 nm absorption band			350 nm absorption band		
	Wavelength λ(nm)	Wave No $\bar{v}$ (cm^{-1})	Molar Extinction Coefficient ε(λ) ($LM^{-1}cm^{-1}$)	Wavelength λ(nm)	Wave No (cm^{-1})	Molar Extinction Coefficient ε(λ) ($LM^{-1}cm^{-1}$)
1	240.17	4.16E+06	319.81	320.51	3.12E+06	1506.94
2	245.06	4.08E+06	718.1	324.68	3.08E+06	1851.78
3	250.32	3.99E+06	1012.47	330.03	3.03E+06	2043.98
4	255.20	3.92E+06	1386.85	335.57	2.98E+06	2212.03
5	260.07	3.85E+06	1273.49	340.14	2.94E+06	2190.57
6	265.32	3.77E+06	1819.43	344.83	2.90E+06	2312.79
7	270.18	3.70E+06	1813.36	349.65	2.86E+06	2228.93

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8	275.03	3.64E+06	1785.85	354.61	2.82E+06	2234.59
9	280.26	3.57E+06	2222.92	359.71	2.78E+06	2251.64
10	285.10	3.51E+06	1953.23	364.96	2.74E+06	2208.89
11	290.31	3.44E+06	1778.55	370.37	2.70E+06	2164.49
12	295.14	3.39E+06	1989.85	375.94	2.66E+06	2031.08
13	300.34	3.33E+06	1783.11	380.23	2.63E+06	1920.07
14	305.16	3.28E+06	1567.81	384.62	2.60E+06	1570.15
15	310.34	3.22E+06	1311.47			
16	315.15	3.17E+06	1287.221			

Table 6.2 Oscillator strength and life time for the transitions corresponding to the two bands in the absorption spectrum of potassium dichromate solution.

SN	Absorption band	Area under $\varepsilon(\lambda)$ versus $\bar{\upsilon}$ curve	Wave number at peak of $\varepsilon(\lambda)$	Oscillator strength	Life time
1	257 nm	1.4924×10^{9}	3.56812×10^{6}	6.462	1.83×10^{-14} s
2	350 nm	1.09113×10^{9}	2.9×10^{6}	4.725	3.78×10^{-14} s

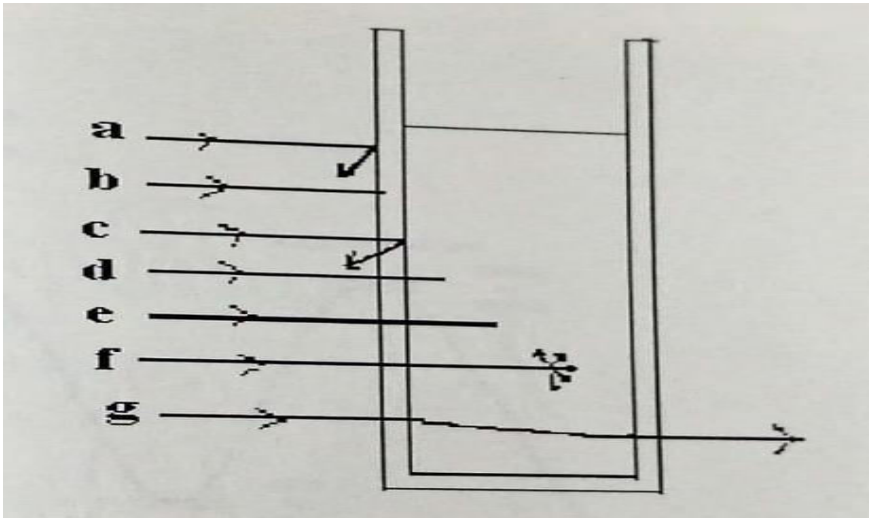

Figure 6.1 The possible attenuation of transmitted light beam in the cell. a: reflection at air/glass interface; b: absorption by glass; c: reflection at glass/solution interface; d: absorption by solute; e: absorption by solvent; f: scatter by solution; g: refraction or dispersion by the cell.

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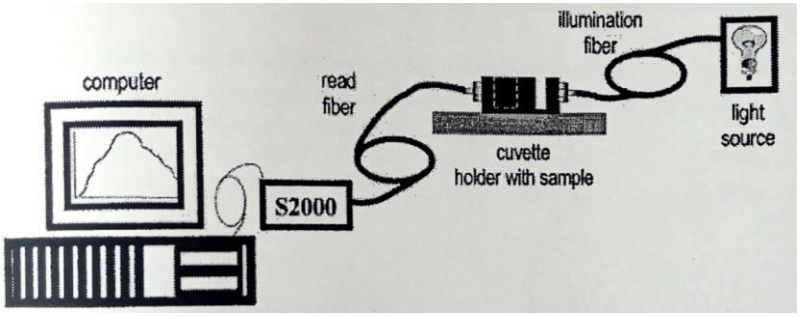

Figure 6.2 Fibre optic spectrometer configurations for recording absorption spectrum.

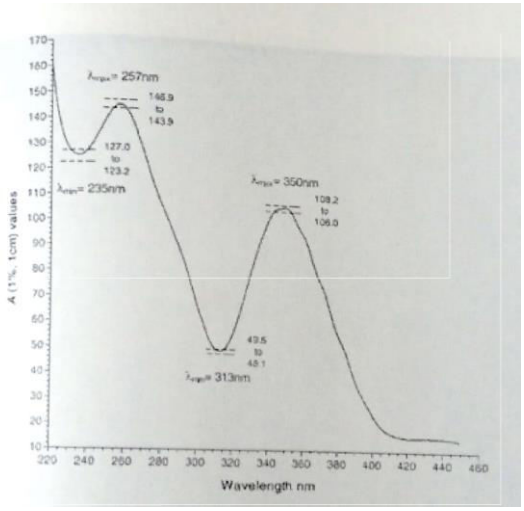

Figure 6.3 Standard absorption spectrum of potassium dichromate in acidic (0.005M sulphuric acid) medium

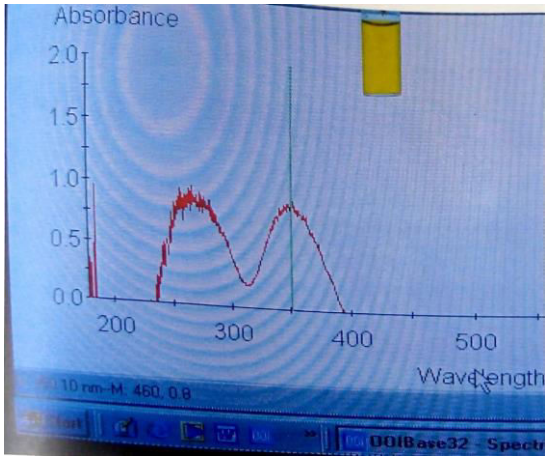

Figure 6.4 Photograph of the PC monitor with absorption spectrum for 0.000266 mole/liter concentration solution (S4). The solution in a tube is held in front of the monitor while taking the shot.

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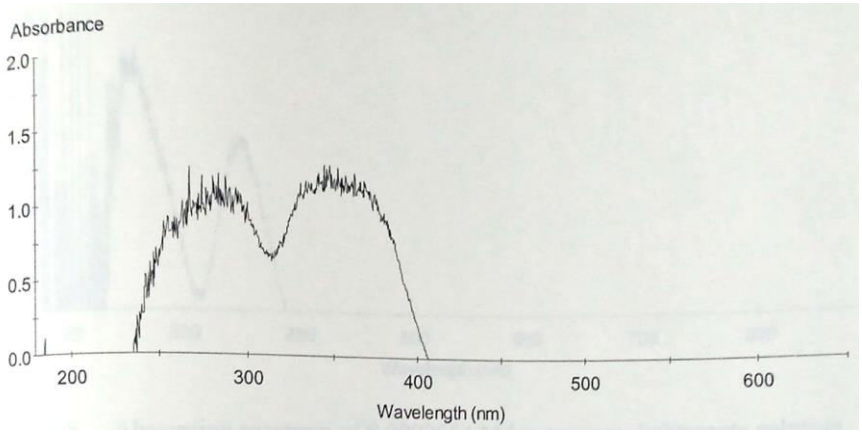

Figure 6.5 Absorption spectrum of 0.000531 M/l potassium dichromate solution.

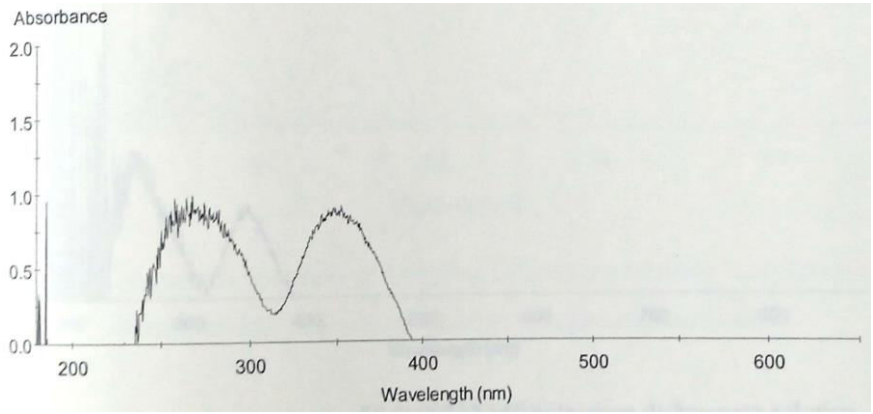

Figure 6.6 Absorption spectrum of 0.000266 M/l potassium dichromate solution.

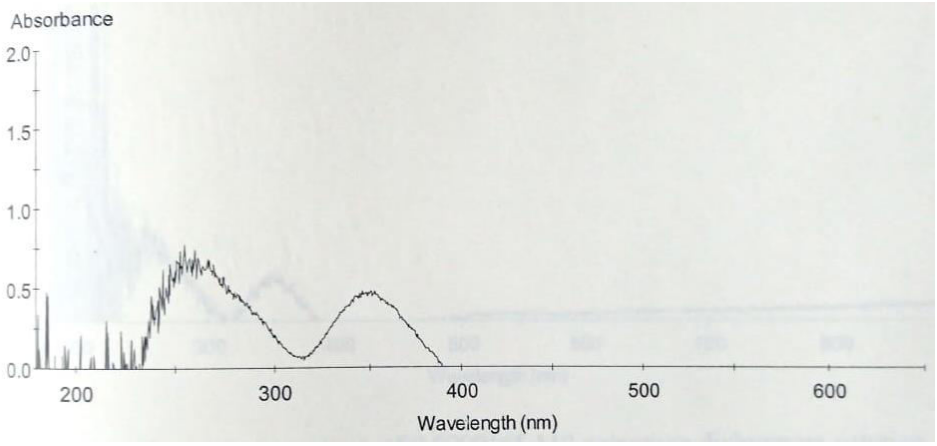

Figure 6.7 Absorption spectrum of 0.000133 M/l potassium dichromate solution.

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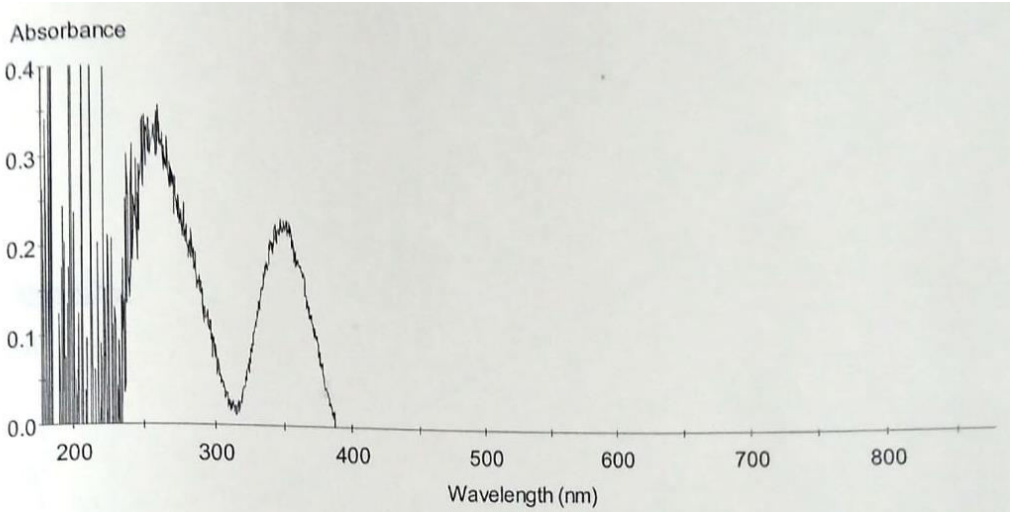
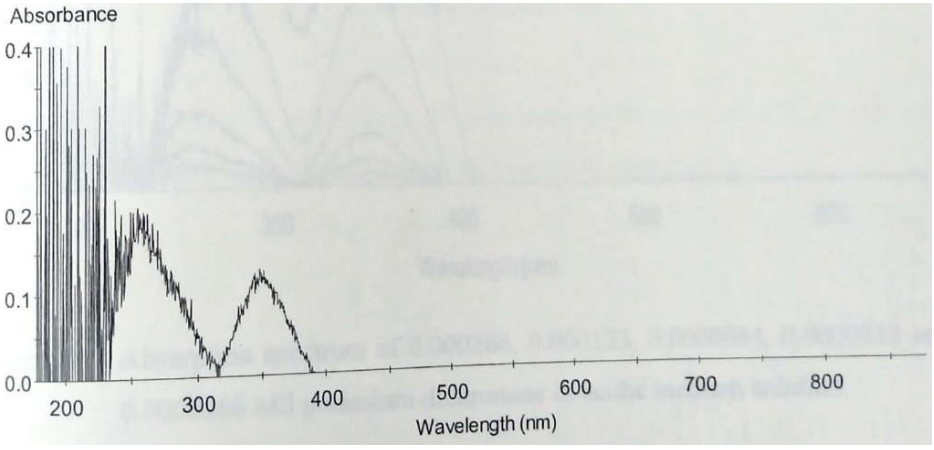


Figure 6.8 Absorption spectrum of 0.0000664 M/l potassium dichromate solution.



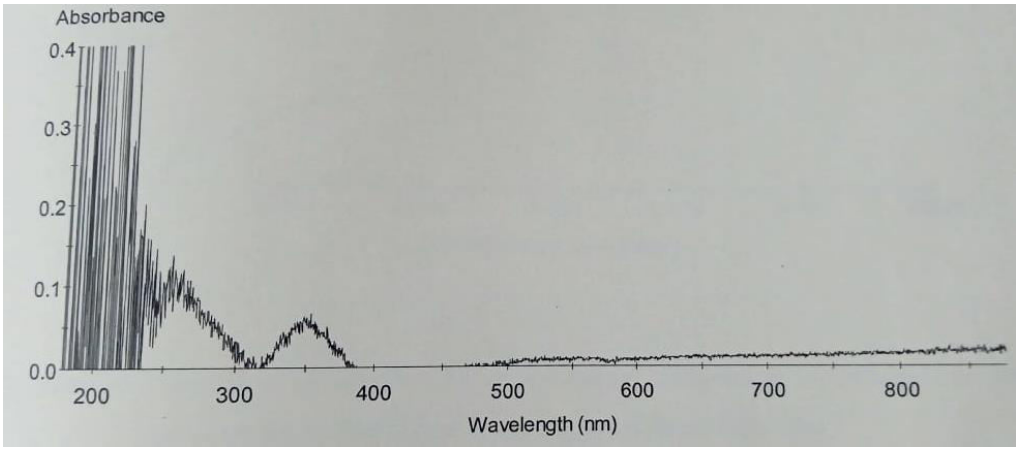


Figure 6.10 Absorption spectrum of 0.0000166 M/l potassium dichromate solution.

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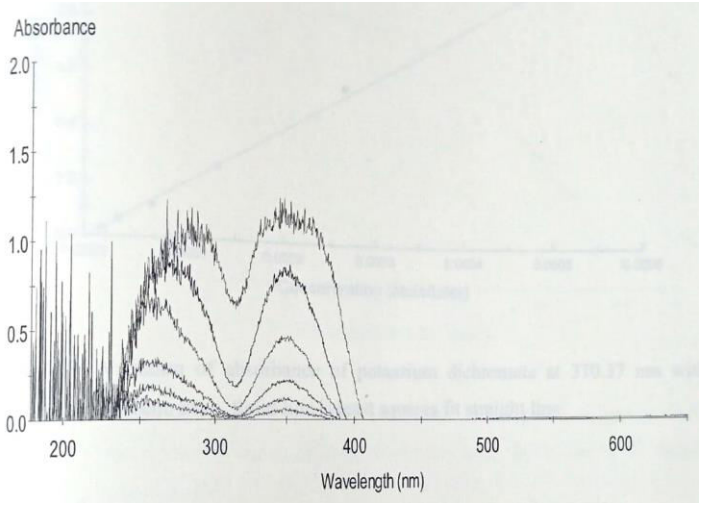

Figure 6.11 Absorption spectrum of 0.000266, 0.000133, 0.0000664, 0.0000332 and 0.0000166 M/l potassium dichromate in acidic medium solution.

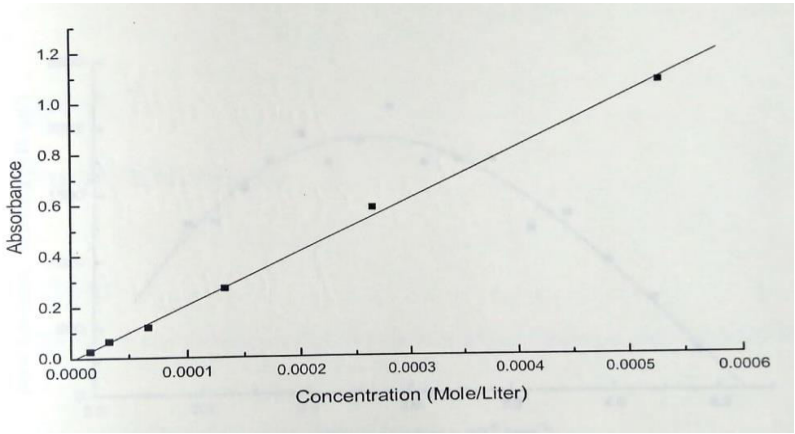

Figure 6.12 Variation of absorbance of potassium dichromate at 370.37 nm with concentration. Solid line is least squares fit straight line

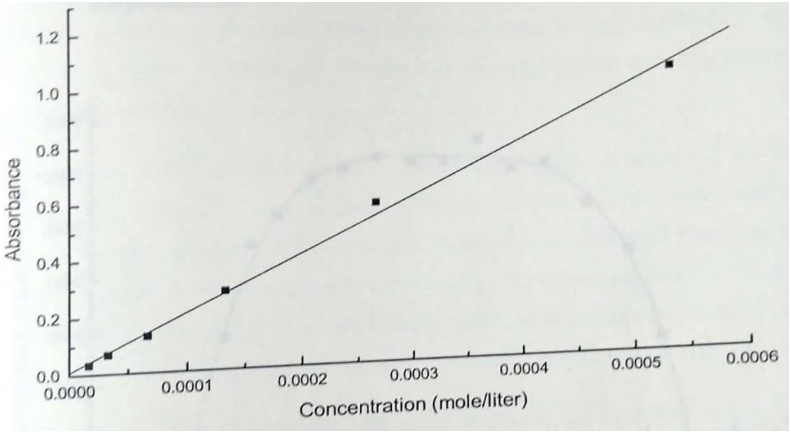

Figure 6.13 Variation of absorbance of potassium dichromate at 295.14 nm with concentration. Solid line is least squares fit straight line.

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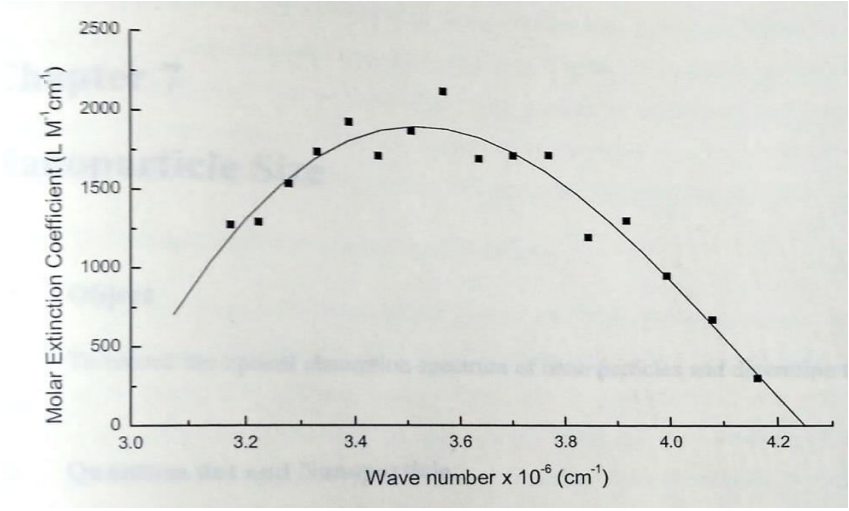

Figure 6.14 Variation of molar extinction coefficient of potassium dichromate with wave number under 257 nm absorption band. Solid line is 4th degree polynomial fit.

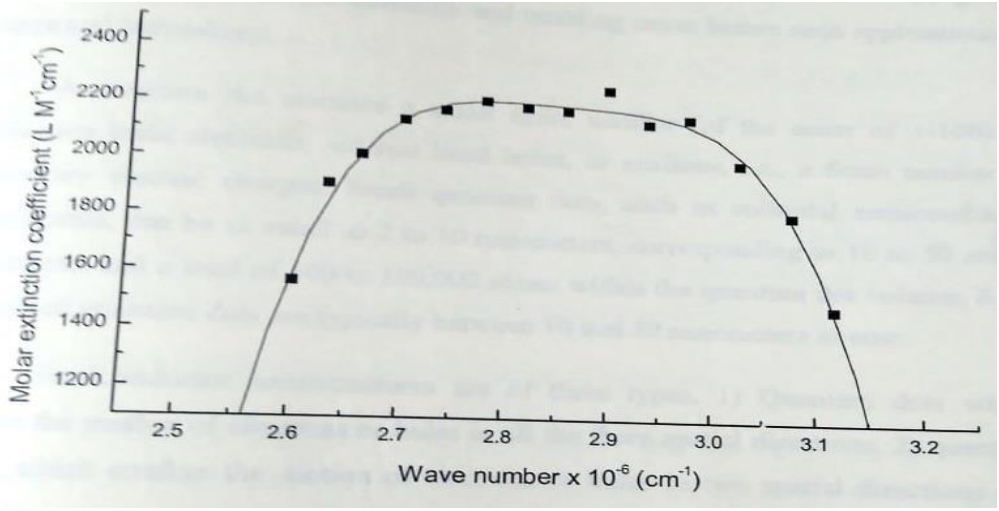

Figure 6.15 Variation of molar extinction coefficient of potassium dichromate with wave number under 350 nm absorption band. Solid line is 4th degree polynomial fit

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