ABSORPTION ANALYSIS OF SOLIDS AND LIQUIDS

1. INTRODUCTION

When a monochromatic light passes through a certain thickness of solid or of a liquid enclosed in a transparent cell, the intensity of the transmitted light may be much smaller than that of the incident light, owing to absorption along its passage. If the wavelength is changed, the amount of absorption will also be changed to a greater or lesser extent.

When absorption measurements are extended over the whole electromagnetic spectrum, it is found that no substance exists which does not show strong absorption for some wavelengths. For a given medium, the intensity of the outgoing beam, \( I_t \), depends on the thickness, \( d \) of the passage according to the exponential law

\[
I_t = I_o \exp(-\alpha d)
\]  

(1)

with \( I_o \) as the incident beam intensity, and \( \alpha \) as the attenuation constant for the material. In general, we can regard \( \alpha \) as being made up of two parts, \( \alpha_s \) due to true absorption, i.e., the actual disappearance of the light and \( \alpha_a \) due to scattering of light.

2. Double-beam spectrophotometer

A double-beam spectrophotometer is employed for the analysis in this experiment. It combines high performance and simplicity of operation with excellent reliability.

Fig.1 shows the optical system of a typical double-beam spectrophotometer. The white light emitted from the light source is transformed into a monochromatic beam by reflecting off a concave diffraction grating (G) with a grating constant of 1/600mm. The beam sent from the monochromator passes through the filter (F), is reflected by the toroidal mirror (M2), and is then separated into reference beam and sample beam by the half mirror (HM). The two beams which have passed through the sample compartments are focused by lenses, and are then irradiated into the detectors (D1&D2) where they are converted into electric signals.
2. EXPERIMENT 1

In this experiment, you are going to use the Shimadzu Recording Spectrophotometer UV-3600. Fig. 2 shows its screen display, its sheet keys and the basic function of each key. The steps in operating this instrument are described briefly in the following. The more details can be learnt from the lecturer in charge.

1) Turn on the power of the spectrophotometer, and the spectrophotometer goes through the initialization automatically. If there is no problem, the CRT of the spectrophotometer show the screen of mode selection.
2) To measure the absorption or transmission spectrum as a function of wavelength in nanometer (nm), press Key 2.
3) To change the start and end wavelength, or change the absorption spectrum to the transmission spectrum, or vice versa, please discuss the detailed steps with the lecturer in charge or the lab demonstrator.

In this experiment, you are required to measure the absorption spectra of a few different colored glasses with wavelengths ranging from 350 nm to 750 nm.

3. EXPERIMENT 2

In this experiment, you are required to verify the Lambert-Beer law experimentally. To do so, you will measure the absorbance as a function of the concentration of Praseodymium Chloride (PrCl₃) in solutions, and then determine the absorptivity.

Fig. 3 shows the Lambert-Beer law. In this scheme, a monochromatic beam with incident intensity \( I_o \) travels through a liquid phase having concentration \( c \) and path length \( d \), which results in the intensity of the monochromatic radiation decreasing to \( I_t \) with

\[
I_t = I_o \times 10^{-\varepsilon c d} \tag{2}
\]

where \( \varepsilon \) is a constant known as absorptivity, which varies depending on the sample. Eq.(2) represents the statement of Lambert-Beer law. The transmittance, \( t \), is defined as the ratio of the transmitted intensity to the incident intensity as follow:

\[
t = \frac{I_t}{I_o} = 10^{-\varepsilon c d} \tag{3}
\]
A common logarithm of inverse transmittance can be expressed as follow:

\[ \log(1/t) = \varepsilon \cdot c \cdot d = E \quad (4) \]

where \( E \) is called the absorbance (ABS).

The experimental procedure is as follows:

1. By repeating the experimental steps outlined in Expt. 1, obtain the absorbance spectra for a Praseodymium Chloride solution. From the absorbance spectrum, determine the absorption peak position in terms of wavelength. (To prepare these solutions, please refer to Section 4 Sample Preparation.)

2. Press Key Mode for returning to the screen of mode selection.

3. Press Key 1 to conduct the photometric measurements. The parameter configuration screen of the photometric measurement will be displayed. To specify the measurement wavelength, use the GOTO WL key.

4. Insert a solution, and press the SART/STOP key, you will obtain its absorbance value.

5. Repeat Step (4) to obtain the absorbance values for different concentrations.

6. Plot the absorbance as function of the concentration to determine the absorptivity.

Note: If the blank correction is required, set the blank sample (pure solvent) prior to the measurement and then press AUTOZERO key. The measured value will be set to zero ABS.

4. PREPARATION OF SAMPLE (Praseodymium Chloride solution)

By dissolving a suitable amount of Praseodymium Chloride (PrCl\(_3\).7H\(_2\)O) in water, we can obtain several concentrations (mol/l) of the solvent. An example of concentration calculation is presented below for clarity.

Calculation:

<table>
<thead>
<tr>
<th>Atomic mass</th>
<th>140</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic mass</td>
<td>35</td>
</tr>
<tr>
<td>Atomic mass</td>
<td>18</td>
</tr>
</tbody>
</table>
Molar mass of PrCl₃·7H₂O : 371g
Molar mass of PrCl₃ : 245g

Wt of H₂O in each mole of PrCl₃·7H₂O : 126g (or 0.126 litre)

(Hence for every mol of PrCl₃·7H₂O, we need to mix it with 1-0.126 litre of water to obtain a concentration of 1 mol/l. of PrCl₃)

<table>
<thead>
<tr>
<th>Conc (mol/l) of PrCl₃</th>
<th>Wt of PrCl₃·7H₂O (g)</th>
<th>Vol. of H₂O (l) added</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>37.1</td>
<td>0.9874</td>
</tr>
<tr>
<td>0.2</td>
<td>74.2</td>
<td>0.9748</td>
</tr>
<tr>
<td>0.3</td>
<td>111.3</td>
<td>0.9622</td>
</tr>
<tr>
<td>0.4</td>
<td>148.4</td>
<td>0.9496</td>
</tr>
</tbody>
</table>

Fix the volume of water to 3 ml using the bottle-top dispenser, calculate the amount of PrCl₃·7H₂O required to form different concentrations of the solution in the range 0.1 to 0.5 mol/l. Prepare these solutions as your reference standards.

WI lamp -------------------------------------- Tungsten iodide lamp (VIS)
D2 lamp ----------------------------------- Deuterium discharge lamp (UV)
M1 ---------------------------------------------------- Condensing mirror
S1 -------------------------------------------------------- Entrance slit
G ------------------------------------------ Toroidal diffraction grating
S2 ----------------------------- Exit slit
F ------------------------------------------ Filter
M2 ---------------------------------------------------- Toroidal mirror
HM ---------------------------------------------------------- Half mirror
M3, M4 ---------------------------------------------------------- Mirrors
L1, L2 -------------------------------------------------------- Lenses
D1, D2 ------------------------------- Detectors (silicon photodiodes)

Fig. 1 Optical System of Hitachi Model U-2000 Double-Beam Spectrophotometer