SPECTROSCOPY

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Chemistry Lab III

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Every honest researcher I know admits he's just a professional amateur. He's doing whatever he's doing for the first time. That makes him an amateur. He has sense enough to know that he's going to have a lot of trouble, so that makes him a professional.

— Charles F. Kettering (1876-1958) (Holder of 186 patents)

ACKNOWLEDGEMENTS

I express my sincere gratitude to our instructors, Dr. K. S. Viswanathan and Dr. K. R. Shamasundar, for bringing the subject to life and helping us discover, in depth, the science behind the procedures.

I also thank Vivek Sagar (MS11017) for his contribution to this report as my lab-partner, who made the task of performing experiments immensely comfortable and productive at the same time.

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INTRODUCTION TO INFRA RED AND ULTRAVIOLET - VISIBLE SPECTROSCOPY

August 9, 2012

1.1 OBJECTIVE

To

1. understand the method of Fourier Transformed Infrared and Ultraviolet spectroscopy
2. understand the preparation substances for analysis
3. handle and operate the Spectroscopes provided

1.2 THEORY

1.2.1 *Basic Concept*

To find the presence of elements and/or compounds within a given substance, we can use spectroscopy techniques, specially when their concentrations are small and they satisfy certain requirements. The essential idea behind this measurement comes from the fact that elements/compounds absorb lights of certain frequencies to get to a higher energy state. These frequencies are mostly discrete as they correspond to quantized energy levels. This energy could be absorbed for, say, changing the vibrational energy (IR Spectroscopy) or for exciting an electron in the substance to a higher energy level (UV-vis Spectroscopy). We note here that these quantized energy levels are properties of individual substances and are, for most practical purposes, unique.

How much absorption, well, the limit comes from the sensitivity of the experimental setup and concentration of substance given.

For the analysis to be possible, the first condition is that the substance must *absorb* light incident to it. Granted this, we can obtain an absorption spectrum for the given substance, which behaves like a fingerprint of the substance. This can thus be used to not only identify the compound, but also to quantify it. For identification, in the simplest case, we simply need to observe the frequency corresponding to the peaks in the absorption spectrum and match it with the known/expected substance(s). Quantification harnesses a rather "obvious" law, termed *Beer-Lambert's Law*. In the simplest form, the law

quantifies the intuitive notion; higher the concentration of the analyte, higher is the absorption. The relation is given as

$$T = \frac{I}{I_0} = 10^{-\alpha l} = 10^{-\epsilon l c} \tag{1}$$

where I is intensity of incident light, I_0 is intensity of transmitted light, ϵ is molar absorbtivity, l is the optical path length, and c is molar concentration.

1.2.2 *Infra Red Spectroscopy*

Infra Red spectroscopy usually deals with energies of the level that cause change in vibrational energies. The wavelength ranges from 2.5μm to 25μm (4000cm^{-1} to 400cm^{-1}). These energies are characteristic for different bonds which is how, using the spectrum, we can identify (and quantify) the bonds present and thus the compound.

The way the spectroscope works for Infra Red, is rather interesting and ingenious. The setup uses a Michelson interferometer.

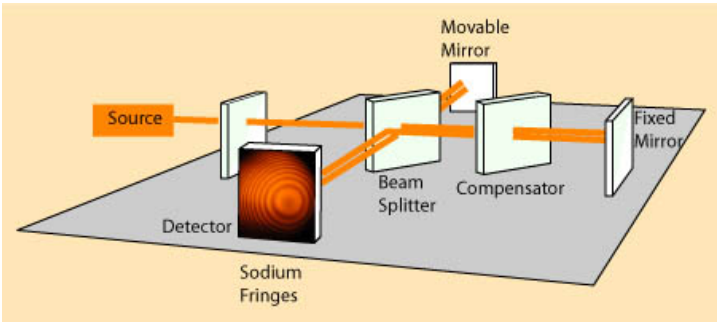


Figure 1: Michelson Interferometer [**?**]

Coherent means phase locked and Monochromatic means single frequency

Before complicating things, let us assume that the source of light is coherent and monochromatic. Now in the Figure 1, we assume the source of light to be the light transmitted through the sample to be analysed. Say the interference at the detector is, at the given configuration, constructive. If we move the movable mirror by $\lambda/4$, where λ is the wavelength of the light, then the detector will receive a dark, destructive interference. If we plot the intensity at the detector as a function of displacement of the moveable mirror, we will, in this case, receive a sine wave.

Note the fact that here, the measurement is simultaneous!

Now let us crank it up a notch. Let us consider the light to still be coherent, but not monochromatic. Let the source of light contain all the transmitted frequencies. Now if the intensity is plotted against the displacement of the moveable mirror, we will get a superposition of sine waves, and we already know how to decompose them to find individual frequencies using *Fourier Transformation*. This essentially

gives us the spectrum, with wavenumber (dimensions of one over distance) on one axis, and intensity on the other.

The source of infra-red light is a Silicon Carbide rod, that is heated to produce the desired radiations. The detector is capacitive, or so we were told.

How is SiC coherent?

1.2.3 *Ultraviolet-Visible Spectroscopy*

Here the wavelengths range from 200nm to 900nm. This range is often in the range of differences of electronic energy levels. The light source is a Tungsten-Neon lamp. In this technique, usually movable diffraction grating is used to split the transmitted light into its component frequencies, "one" of which goes to an intensity detector. Which component is detected depends on the orientation of the diffraction grating. Using this information, an intensity vs. frequency plot is generated which is the desired spectrum.

It must be noted here that the process of moving the orientation of the grating, requires time, which means that the measurement for various frequencies' intensities is not simultaneous, which in certain cases might not be suitable. One solution to such a problem is the use of multiple (arrayed) detectors. Yet it doesn't explain why a Michelson interferometer can't be used in this case. The answer to this comes from the fact that the wavelength in this case is much smaller, thereby complicating the task for preparing reflectors.

Wouldn't the ordinary mirrors for "visible light" suffice?

1.3 EXPERIMENTAL DETAILS

For this session, both IR and UV-visible spectroscopy techniques were demonstrated to us in groups of two. For IR spectroscopy, we used KBr as the base and Benzoic Acid as the analyte. For UV-vis, we used water as the base and $KMnO_4$ as the analyte.

1.3.1 *Infrared*

Procedure

The general procedure is as follows:

A. Weighed 100mg of KBr and ground it well.

B. Transferred it the dye (palletizing module).

C. Converted it into a pellet using the Hydraulic Press (about 8 tons of pressure).

D. Did IR spectroscopy.

E. Weighed 100mg of KBr and with it, 2mg of sample (in this case Benzoid Acid) and repeated from item B.

Details about the IR spectroscopy are as follows:

A. Ran the background to get rid of noise.

B. Did the accumulation 16 times (set the option).

C. Subtracted the first spectroscope from the second

Observation

Detected the carboxylic group (peaks for OH and $C = O$)

1.3.2 *UV-Vis*

Procedure

The general procedure is as follows:

A. Took a suitable amount of water.

B. Did UV-Vis spectroscopy.

C. Again took water and added a suitable amount of $KMnO_4$ and mixed it well.

D. Did UV-Vis spectroscopy.

Details about the UV-vis spectroscopy is corresponding to the previous section.

Observation

Peaks were detected in the range 520nm-550nm, complimentary to Purple as expected.

1.4 ACKNOWLEDGEMENTS

I thank the PhD students, Ms. Shruti and Ms. Shilpa, who helped us with the session and performed the experiment. They also walked us through the procedure for using the apparatus.

2

EXPERIMENT 1A: UV-VISIBLE SPECTROSCOPY

August 16, 2012

2.1 OBJECTIVE

To

1. prepare 10, 25, 50 and 75 ppm solutions of Benzoic Acid in water
2. use one of these for obtaining a spectrogram
3. use three of these for calibration and find the concentration of the third experimentally

2.2 THEORY

This section is the same as and has been covered in the previous experiment.
A few simple relations must be stated however, for clarity. Transmissivity or Transmission (T) is related to observables by Equation 2, where I is intensity of the light transmitted, I_0 is intensity of incident light, ϵ is extinction coefficient, l is the path length and c is concentration of the solution.
Relation between Absorbance (A) and intensity of light is as given by Equation 3. Clearly, A has a linear relation with ϵ as given by Equation 4 and we'll use this very relation to find the concentration of the 'unknown' sample.

$$T = \frac{I}{I_0} = 10^{-\epsilon l c} \tag{2}$$

$$A = -\log 10(\frac{I}{I_0}) \tag{3}$$

$$A = \epsilon l c \tag{4}$$

2.3 PROCEDURE

1. First calculated the mass of Benzoic Acid required for making a 25mL a 250 ppm solution in water, to be *6.25 mg*.

Just in case, $1ppm = 1uL/mL$

Mass of salt	0.0066	g
Mass of paper	0.0001	g
Mass of Benzoic Acid	6.5	mg
Concentration of Benzoid Acid Used	$\frac{6500}{25} = 260$	ppm

Table 1: For the Stock Solution of Benzoic Acid

10 ppm	$\frac{50}{260} = 0.192$	mL
25 ppm	$\frac{125}{260} = 0.480$	mL
10 ppm	$\frac{250}{260} = 0.961$	mL
10 ppm	$\frac{50}{375} = 1.442$	mL

Table 2: For varying concentrations of Benzoic Acid Solution

Used the upper meniscus consistently *for volume measurements*

But does that mean it wouldn't affect the result?

2. Weighed roughly the calculated amount of Benzoic Acid and transferred it to a volumetric flask of 25mL, and made the volume 25mL. This solution is henceforth referred to as the stock solution.
3. Calculated the volume of the stock solution required to prepare 10, 25, 50 and 75 ppm, 5 mL Benzoic Acid solutions.
4. Using a graduated pipette, measured the precise volume in accordance with the calculations and transferred it to a 5mL volumetric flask, and filled it to 5mL of water. Repeated this step for all four concentrations and labelled the flasks accordingly.
5. Calibrated the spectroscope with water first to suppress noise, if any.
6. Used one of the concentrations to generate a spectrogram.
7. Identified the maximum wavelength for use in Beer-Lambert law.
8. Used three of the concentrations to calibrate and fourth as an unknown, using the spectroscope.
9. Printed the spectrogram and noted the observations off of the screen for the known and unknown concentrations.

2.4 CALCULATIONS AND MEASUREMENTS

Refer to Table 1 for the stock solution and to Table 2 for the variants.

WAVELENGTH (λ)	ABSORBANCE
544.00nm	1.710
524.00nm	1.915

Table 3: Wavelengths Absorbed

CONCENTRATION (c)	ABSORBANCE
75ppm	1.902
50ppm	0.971
10ppm	0.237

Table 4: Absorption for various Concentrations

2.5 SPECTROSCOPIC OBSERVATIONS AND ANALYSIS

The maximum wavelength (λ_{max}) was found to be 524.00nm. Refer to Table 3. The Absorbance (A) for various concentration is given in Table 4

Absorbance of 'unknown' sample (25 ppm): 0.489

In accordance with the application, the best fit for the three points was not linear and the concentration of the unknown sample was calculated to be 30.0720 ppm which amounts to a 20% error.
In accordance with least square straight line fit, we get the slope as 0.0249395 $\pm$ 20.34 % but the intercept as -0.0856124 $\pm$ 310.2%. In accordance with these numbers, the concentration works out to be 16.174 ppm, which is 35% off. Refer to Figure 2 for details.

Expected accuracy is 2 – 3%

2.6 DISCUSSION

The accuracy of this experiment, as told by our instructor, is expected to be less than 3%. Since we clearly failed at achieving that number, we analyse in this section, what could've caused the enormous error.

The error could be caused by making errors in any of the following processes

1. Weighing
2. Volume measurement
    a) Pipetting
    b) Filling the Volumetric Flask

Despite taking sufficient care, even if one of the steps mentioned above go wrong, for even one of the samples, since the number of samples for calibration is just three, the entire experiment can, and in this case, did go wrong.

Thus for ensuring such errors do *not* crop up in the future, we can attempt the following

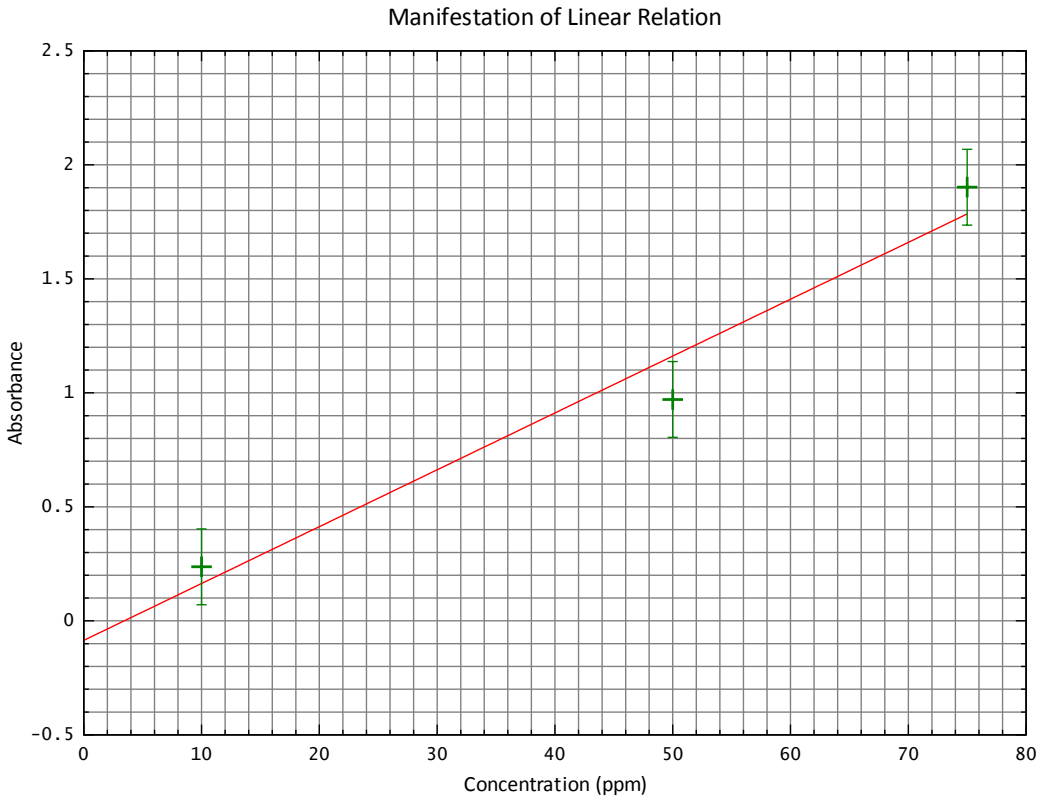
1. Weighing:
    a) Put the paper on the weighing scale and tare it
    b) Add the required amount of substance ensuring nothing gets wet
    c) Keep the container, viz. Volumetric Flask, with accessories, viz. Funnel etc. near the setup
    d) After transferring the contents, weigh the paper again to ensure everything got transferred
2. Volume Measurement
    a) Pipetting
        i. Read the upper meniscus consistently (for this experiment and in general for opaque solutions)
        ii. Use graduated pipettes that can provide sufficient precision
        iii. *Ensure the liquid doesn't stick on the walls*
    b) Filling Volumetric Flask
        i. Again, use the upper meniscus
        ii. Use a dropper to add towards the end to avoid accidentally adding extra volume

This is most likely what went wrong!

2.7 ACKNOWLEDGEMENTS

I thank Ms. Sumyra, the PhD student, who helped us with the use of the spectroscope. I also acknowledge the contribution of Ms. Athira J. Nair and Mr. Arpit Porwal for the performance of the experiment as team members.

Experiment: UV-visible Spectroscopy




```
Slope of Best Fit Line          : +0.1663
Intercept of Best Fit Line      : +0.0249
```

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Performed on: August 16, 2012
Performed by: Athira, Arpit and Atul
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Figure 2: Least Square Fit

3

EXPERIMENT 1B: INFRA RED SPECTROSCOPY

August 23, 2012

3.1 OBJECTIVE

To study the spectroscopic characteristics of atleast three of the following compounds using an FTIR spectroscope.

1. Benzoic Acid
2. Naphthalene
3. Urea
4. Thio-Urea
5. Salicylic Acid

3.2 THEORY

This section is the same as and has been covered in the previous experiment Chapter 1.

3.3 PROCEDURE

1. Weighed approximately 200mg of KBr and $2-4$mg of sample and ground it well using mortar and pestle. (Didn't use any sample for the first time, to use for baseline correction.)
2. Transferred the powdered contents into the palette maker and put it inside the hydraulic press
3. Applied about $6-8$tons of pressure for $30-60$ seconds. Released the pressure after, and transferred the contents to the palette holder.
4. Placed the palette holder into the FTIR spectroscope and scanned it (in case of the first palette, background scanned it).

The process must be done quickly to avoid accumulation of moisture.

3.4 ANALYSIS

1. Urea - Table 5

N – H stretching	3399.69	cm^{-1}
C = O stretching	1669.64	cm^{-1}
N – H bending	1625.39	cm^{-1}

Table 5: IR peaks for Urea

C – H stretching	2832.14	cm^{-1}
O – H stretching	2554.86	cm^{-1}
C = O stretching	1694.66 and 1699.26	cm^{-1}

Table 6: IR peaks for Benzoic Acid

2. Benzoic Acid - Table 6
3. Thio Urea - Table 7
4. Naphthalene - Since there are no functional groups, according to L. G. Wade's *Organic Chemistry*, peaks are expected to be observed in the following ranges
   a) For Naphthalene in general:
      i. between 3000 and 3100
      ii. between 1570 and 1650

      Corresponding observations are given in Table 8

What does alpha mean structurally in this case?

   b) For *alpha* naphthalene, we have
      i. between 1375 and 1425
      ii. between 750 and 810

      Corresponding observations are given in Table 9
   c) For *beta* naphthalene, peaks are expected to be in the ranges:
      i. less than 700
      ii. between 800 and 860

      These were found to be absent.

3.5 DISCUSSION

For this experiment, even though we knew which compounds we're taking, after printing the spectrographs, we didn't label them to see if

NH_2 stretching	3368.14	cm^{-1}
NH_2 bending	1588.41	cm^{-1}
C = S stretching	1092.87	cm^{-1}

Table 7: IR peaks for Thio-Urea

3061.97	cm^{-1}
3048.41	cm^{-1}
3029.35	cm^{-1}
1651.94	cm^{-1}
1634.25	cm^{-1}
1592.53	cm^{-1}

Table 8: IR peaks for Naphthalene

1383.98	cm^{-1}
782.47	cm^{-1}

Table 9: IR peaks for *alpha* Naphthalene

they could be identified by matching them with their expected peaks. This method does in fact work quite accurately and the fingerprint region was also observed to match, when compared with known spectrographs. I have still not been able to understand the meaning of alpha and beta structures of Naphthalene, which I so far believe to not exist. However, experimentally, in accordance with the literature, the structure seems to be alpha.

3.6 ACKNOWLEDGEMENTS

I acknowledge the contribution of Mr. Arpit Porwal for the performance of the experiment as a team member. I would also like to thank Mr. Biplob Nandy and Ms. Saumya Gupta for exchanging results to mutually provide scope for wider analysis.
I am grateful to Mr. Arjit Kant Gupta who helped me with the analysis and conformation of the results by sharing his spectrographs of known compounds.
I also thank L. G. Wade for the book “Organic Chemistry” which was used to look up the expected IR peaks in the compounds analysed.

Part II

THE SHOWCASE

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