Statistical Thermodynamics Approach to Urinary Analysis Employing Micro-Canonical Ensemble

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Abstract– **This paper presents, the study of urinary analysis using micro-canonical ensemble, which dealt with the study of urine system that was further related to the micro-canonical ensemble of statistical thermodynamics. The goal of statistical thermodynamics is to understand and to interpret measurable macroscopic properties of the absorbance and to establish valid relationships among measureable variables in a statistical manner over samples range. A valid relationship with constant, k_B between the absorbance (A_{abs}) and wavelength (λ) of different samples was obtained. The use of numerical method "Newton Cotes methods" to integrate the absolute values of absorbance (A_{abs}) and wavelength (λ) was equally employed. This study is necessary to show the relationships among important variables for optimal outputs and longevity of the system. Absolute values of absorbance (A_{abs}) and wavelength (λ) are 12.32 and 497.143Å, respectively.**

Keywords– **Absorbance, Intensity, Micro-canonical Ensemble, Spectrometer, Statistical thermodynamics, Urine system, Urinary analysis and Wavelength**

I. INTRODUCTION

A spectrometer consists of two instruments, namely, a spectrometer for producing light of any selected colour (wavelength), and a photometer for measuring the intensity of light [1]. The instruments are arranged so that liquid in cuvette can be placed between the spectrometer beam and the photometer. The photometer delivers a voltage signal to a play device normally a galvanometer. The signal changes as the amount of light absorbed by the liquid changes [1]. Development of colour is linked to the concentration and can be measured by determining the extent of absorption of light at the appropriate wavelength [1]. A spectrometer is used to measure the intensity of the light entering a sample and the light exiting a sample and compares the two intensities.

The information about the two intensities can be expressed as transmittance (the ratio of the intensity of the existing light to the entering light) or percent transmittance (%T). Different materials absorb different wavelengths of light [2], [3]. Therefore, the wavelength of maximum absorption by a material is one of characteristic properties of that material. Many compounds absorb ultraviolet (UV) or Visible (Vis) Light. The amount of radiation absorbed may be measured in a number of ways [3], [4]:

Transmittance, $T = \frac{P_o}{P}$ (1)

% Transmittance, $\%T = 100T$ (2)

Absorbance; $A = Log_{10}\frac{P_o}{P}$ (3)

$A = Log_{10}\frac{1}{T}$ (4)

$A = Log_{10}\frac{100}{\%T}$ (5)

The %T can be related to the absorbance (A) by the equation below [1], [3]:

$A = 2 - [log(\%T)]$ (6)

The essential task in this application of statistical thermodynamics is to determine the distribution of a given amount of Absorbance over N identical systems.

The goal is to understand and to interpret the measurable macroscopic properties of materials in terms of the properties of their constituent particles and the interactions between them. To obtain the absolute Absorbance value of Urine over range of wavelengths. To statistically collect data of absorbance and analyze the system using statistical thermodynamics ensemble. These values obtained are applied to the micro-canonical ensemble with the intent to ultimately establish a relationship between absorbance (A) and the wavelength with a possible constant k, thus defining a mathematical relationship between these parameters.

A. Underlying Theory

When monochromatic light (light of a specific wavelength) passes through a solution, there is usually a quantitative relationship (Beer's law) between the solute concentration and the intensity of the transmitted light [1], [2], [4].

$I = I_o log_{10^{-kl}} = I_o x 10^{-kl}$ (7)

Where; I_o is the intensity of transmitted light using blank water or pure solvent, I is the intensity of the transmitted light when the sample solvent, L = distance the light passes through the solution, k = constant

If the light path is constant, as the case with a spectrometer, Beer's law may be written as:

$I = I_{o^{-Kl}} = T$ (8)

Where; K is a new constant, T = transmittance of the solution

There is a logarithmic relationship between transmittance and concentration of the coloured compound [1]:

$$-logT = log\frac{1}{T} = Kc = Optical\ Density(O.D) \qquad (9)$$

The optical density (O.D) is directly proportional to the concentration of the coloured compound. Most spectrometer has a scale that reads both in O.D (Absorbance) units which is a logarithm scale and in % transmittance which is arithmetic scale. Beer Lambert law is the linear relationship between absorbance and concentration of an absorbing species. It is usually written as [5]:

$$A = a(\lambda)bc \qquad (10)$$

Where; A = Measured Absorbance, a(λ) = wavelength dependent absorption coefficient, b = path length, c = Analyte concentration.

II. MATERIALS AND METHODS

A. The Apparatus

The apparatus include the following: Universal Container/tube, Digital Calorimeter, Microscope, Disposable Hand gloves, Urine Samples (A-J), Distilled water and Test Stripe.

B. Experimental Procedures

Step1: Various samples of urine A-J were collected and cultured so as not to allow the growth of bacteria.

Step2: Set the digital calorimeter at a particular wavelength level.

Step3: Select appropriate filter and switch on the shutter.

Step4: This is followed by inserting the test tube with blank solution made from distilled water in the tube holder:

i. Set instrument to zero level (i.e. 00) on display by adjusting Optical Density (O.D) through the control knob.

ii. Then replace blank sample solution with cultured sample A in tube hold.

iii. Read optical density value on display to get the absorbance.

iv. Repeat procedure ii-iii for samples B-J

v. Plot the graph of various wavelengths against Absorbance for each sample A-J.

III. DATA PRESENTATION

Table 1: Experiment Result

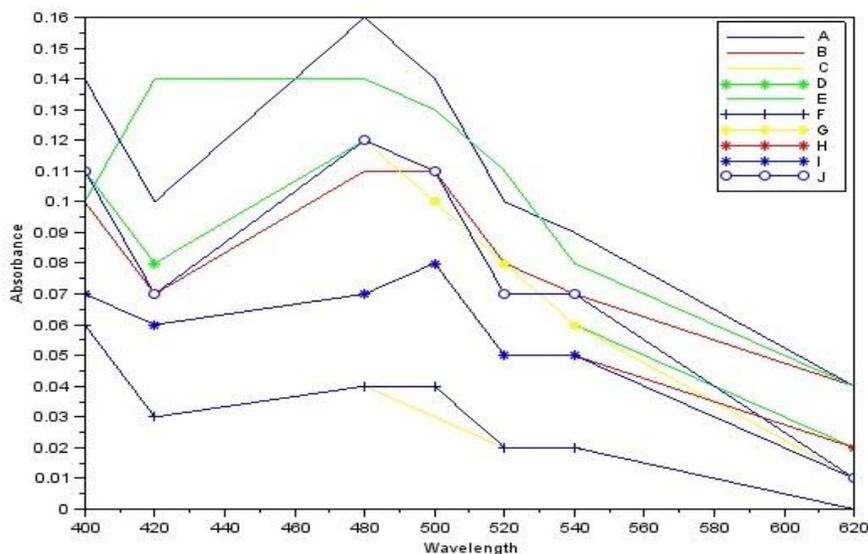| Wavelength(Å)	A	B	C	D	E	F	G	H	I	J
400	0.14	0.1	0.06	0.11	0.1	0.06	0.11	0.07	0.07	0.11
420	0.1	0.07	0.03	0.08	0.14	0.03	0.07	0.06	0.06	0.07
480	0.16	0.11	0.04	0.12	0.14	0.04	0.12	0.07	0.07	0.12
500	0.14	0.11	0.03	0.1	0.13	0.04	0.1	0.08	0.08	0.11
520	0.1	0.08	0.02	0.08	0.11	0.02	0.08	0.05	0.05	0.07
540	0.09	0.07	0.02	0.06	0.08	0.02	0.06	0.05	0.05	0.07
620	0.04	0.04	0	0.02	0.04	0	0.01	0.02	0.01	0.01

Fig. 1: Graph of Absorbance against Wavelength

The plot in Fig.1 reveals a stimulating pattern for urinalysis. The absorbance of the respective ten samples decreased from wavelength 400Å - 420Å, except sample E which showed an increased value in its response from wavelength 400Å - 420Å. The increase in the value of absorbance E recorded is obviously a faulty one. This could be explained against the possibility of some experimental error or the higher level of glucose in the urine which could lead to diabetes. The absorbance of respective ten samples further steeply increased as the wavelength increased until a critical wavelength of 480Å, (except sample I which increased until 500Å), where the peak value was attained. A further increase in the wavelength saw a steep decrease in the absorbance values. The peak values of absorbance are of the range $0.042 \leq A \geq 0.16$.

A. Data Analysis and Application

Using the data as presented in table 1 to integrate the absolute value of absorbance by the application of SciLab mathematical solution model and integrating between the minimum and maximum wavelength, the absolute absorbance can be determined as shown in equation 11.

$$A_{abs} = \int_0^\infty A d\lambda \qquad (11)$$

Where; 0 = minimum value, ∞ = maximum

Applying Newton Cotes trapezoidal methods to the system:

For 'n' equally spaced base points, the Newton-Cotes closed integration formula is given by [7]:

$$A_{abs} = \int_0^\infty A d\lambda = \int_a^b w(x)F(x)\,dx$$
$$= \sum_{k=0}^n \lambda_{\bar{k}} f_{\bar{k}} \qquad (12)$$

Where $\lambda_{\bar{k}}$ is weighting coefficient, x are the base points that are equally spaced, and n is the number of base points (or n-1 is the number of intervals);

$$A_{abs} = \int_0^\infty A d\lambda = \int_a^b F(x)\,dx$$
$$= \frac{b-a}{2}[F(a) + F(b)] \qquad (13)$$

Where F(x) = A, dx = dλ, a = minimum limit, and b = maximum limit

$$F(a) = \sum_{i=1}^n \left[\left(\frac{A,B,C,\ldots J}{n}\right)_1 \right] \qquad (14)$$

$$F(b) = \sum_{i=1}^n \left[\left(\frac{A,B,C,\ldots J}{n}\right)_8 \right] \qquad (15)$$

$$A_{abs} = \int_0^\infty A d\lambda = \frac{620-400}{2}[0.093 + 0.019]$$
$$= 110[0.112]$$

$$\mathbf{A_{abs}} = 12.32$$

Applying Regression approach to the system:

$$A_{abs} = A(\lambda) \qquad (16)$$

Let the approximating polynomial be given by [7], [8]:

$$A = \propto_0 + \propto_1 \lambda + \propto_2 \lambda^2 \qquad (17)$$

Define a variable X $= \begin{pmatrix} 1 & \lambda_o & \lambda_o^2 \\ 1 & \lambda_1 & \lambda_1^2 \\ 1 & \lambda_2 & \lambda_2^2 \\ 1 & \lambda_3 & \lambda_3^2 \\ . & . & . \\ . & . & . \\ 1 & \lambda_n & \lambda_n^2 \end{pmatrix}$ such that; $A_{abs} = [X] \begin{pmatrix} \propto_o \\ \propto_1 \\ \propto_2 \end{pmatrix}$;

$$A_{(abs)i} = \begin{pmatrix} 1 & 400 & 160,000 \\ 1 & 420 & 176,400 \\ 1 & 480 & 230,400 \\ 1 & 500 & 250,000 \\ 1 & 520 & 270,400 \\ 1 & 540 & 291,600 \\ 1 & 620 & 384,400 \end{pmatrix} \begin{bmatrix} \propto_o \\ \propto_1 \\ \propto_2 \end{bmatrix}$$

$\propto_0 = 0.1575, \propto_1 = -0.0002, \propto_2 = 0.0000$

Therefore;

$$A = 0.1575 - 0.0994\lambda \tag{18}$$

$$A_{abs} = \int_{400}^{620} A d\lambda = \left[0.1575\lambda - 0.0994 \frac{\lambda^2}{2} \right] = 12.21$$

Comparing the absolute values of Absorbance "A_{abs}" using both Newton-Cotes Quadrature and Regression approach, it was observed that the absolute values are approximately equal. Since the time is constant, using the table of values, the regression equation is obtained as shown above.

Assume path length "b" and analyte concentration to be "unity (1)"; $A_{abs} = a(\lambda)$

$$a = \frac{A_{abs}}{\lambda} = \frac{12.32}{497.143} = 0.025 = absorption\ coefficient \tag{19a}$$

Therefore;

$$A_{abs} = 0.025\lambda bc = 12.43 bc \tag{19b}$$

B. Application of Statistical Thermodynamics Ensemble to the System

The system described above is an isolated system thus microcanonical ensemble is implied. Since the second law of thermodynamics applies to isolated systems, the microcanonical ensemble also describes an isolated system.

In micro-canonical ensemble, (Total number of particles "N", Volume of the system "V" and Total energy of the system "E") are fixed.

Because an isolated system keeps a constant energy, the total energy of the system does not fluctuate. Thus, the system can access only those of its micro-states that correspond to a given value E of the energy. The internal energy of the system is then strictly equal to its energy [9];

$$E(S,V) = U(S,V) \tag{20}$$

Let $\Omega(E)$ the number of micro-states corresponding to this value of the system's energy. The macroscopic state of maximal entropy for the system is the one in which all micro-states are equally likely to occur, with probability $\frac{1}{\Omega(E)}$, during the system's fluctuations [10], [11]:

$$S = -K_b \sum_{j-1}^{\Omega(E)} \left\{ \frac{1}{\Omega(E)} \ln \frac{1}{\Omega(E)} \right\} = K_b \ln [\Omega(E)] \tag{21}$$

The probability P_i that a macroscopic system is in thermal equilibrium with its environment, will be in a given micro-state with energy E_i according to the Boltzmann distribution [8], [10]:

$$P_i = \frac{e^{-\beta E_i}}{\sum_j^{jmax} e^{-\beta E_j}} \tag{22}$$

Where; $\qquad \beta = \frac{1}{KT} \tag{23}$

The temperature T arises from the fact that the system is in thermal equilibrium with its environment. The probabilities of the various micro-states must add to one, and the normalization factor in the denominator is the canonical partition function [10], [11]:

$$Z = \sum_j^{jmax} e^{-\beta E_j} \tag{24}$$

Where; E_i is the energy of the ith micro-state of the system. The partition function is a measure of a number of states accessible to the system at a given temperature.
The probability of finding a system at temperature T in a particular state with energy E_i is given by [9]:

$$P_i = \frac{e^{-\beta E_j}}{Z} \tag{25}$$

Where; $E = \frac{\sum_i E_i e^{-\beta E_i}}{Z} = \frac{1}{Z} \frac{d}{d\beta} \tag{26}$

Since the system does not fluctuate;

$$S = K_b \ln N \tag{27}$$

Since partition function and fugacity relate [8];

$$\mu = K_b T \ln Z \tag{28}$$

Where μ is partition function, Z=fugacity (i.e., the easiness of adding a new particle into the system);

$$S = \frac{\mu}{T}\ln\left(\frac{N}{Z}\right) \qquad (29)$$

Since Temperature "T" is constant throughout and the system does not fluctuate.

Therefore; $\qquad S = \mu_f \ln Z_N \qquad (30)$

Where; μ_f is the new partition function, Z_N is the number of fugacity.

Equations, 28 and 30 shows that, S increases as μ_f increased and both are the functions of fugacity Z, and relating these equations (28, 30) with Equation 10, it was observed that A_{abs} increases as $a(\lambda)$ increased and this practically shows a valid relationship.

IV. CONCLUSION

This paper on the study of urinary analysis using micro canonical ensemble of statistical thermodynamics has further braced the place of the applicability of engineering thermodynamics or at least analytical thermodynamics in discovering solution to various scientific and biomechanics processes.

Sample E, shows an increased value in its response from wavelength 400Å - 420Å, this explains a possible higher level of glucose in the urine. The absorbance of respective ten samples further steeply increased as the wavelength increased until a critical wavelength of 480Å, (except sample I which increased until 500Å), where the peak value was attained. A further increase in the wavelength saw a steep decrease in the absorbance values which explains reduction of sugar level (i.e., absorption coefficient reduces, equations 18 and 19a refer).

This research has really shown the interface between Statistical Thermodynamics and real systems (Closed). The valid relationship between absorbance and wavelength $(A = 0.1575 - 0.0994\lambda)$ and $A_{abs} = 0.025\lambda bc = 12.43bc$ was established.

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