Use of Drude 2014

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Use of a modified Drude's equation to investigate the optical rotation property of sugars

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ABSTRACT

Sugar compounds (glucose, xylose, arabinose, and galactose) and their mixed solutions were examined using the optical rotatory dispersion (ORD) measurement technique with a modified Drude's equation. Commonly, spectroscopic methods utilize the observation of absorption bands which are, in the case of sugars, located in the UV-spectral range. However, the polarization method used in this study allows us to investigate sugar samples in a convenient visible spectral range where sugar solutions are relatively transparent. The ORD set-up can be simple and robust as we will demonstrate: the self-constructed apparatus consists of only two linear polarizers, placed one after the other, with the angle between their transmission axes adjusted to 45°. The sugar solution sample in a cuvette was put between the polarizers. The set-up was connected to a sample compartment of a commercial UV–vis spectrophotometer. The method provided us the specific optical rotation and concentration of sugar solutions with a reasonable accuracy. In addition, the optical rotation value for mixed sugars has been found to be the average optical rotation value of individual sugar content. Beside use in the laboratory environment, the method could also have industrial on-site monitoring applications, for example in bio fuel production.

1. Introduction

Light polarization refers to the fundamental property of an electromagnetic wave – its electric and magnetic fields can oscillate with in more than one direction. The polarization phenomenon is usually described by the oscillation of the electromagnetic wave's electric field. When this field only operates in one plane in space it is denoted as linear polarization. The field can also rotate as the wave propagates (circular or elliptical polarization). The state of polarization can be mathematically described *e.g.* by the Jones or Mueller calculus [1].

Optical polarization is widely exploited in science. The Optical properties of most molecules exhibit directional dependence and thus polarization techniques have been recognized as a powerful tool among scientists in chemistry, biology, and in polymer science to study *e.g.* the assignment of vibrational and electronic transitions, optical activity of oriented molecules, molecular structure and conformation, and the structure of anisotropic media [2].

Furthermore, light polarization is frequently used in geology to study crystalline minerals and in astronomy to observe radiation originating from astronomical sources. As a last example within numerous applications, data transmission using antennas typically relies on the polarization of an electromagnetic wave.

Light polarization has also been utilized in industry for process control and quality inspection purposes. One traditional example can be found in the sugar industry, where polarization based devices, *i.e.* polarimeters, are used for qualitative and quantitative measurements of sugar compounds. In the food, beverage and pharmaceutical industries such devices are exploited in the inspection of the concentration and purity of steroids, vitamins, antibiotics and amino acids among others.

Optical activity refers to a phenomenon where the polarization of light is altered as the electromagnetic wave propagates through a medium – the chiral molecules in the medium turn the orientation of linearly polarized light. The rotation, typically denoted as α, is expressed as degrees. Different molecules exhibit individual rotation power, *i.e.* the specific rotation $[\alpha]$ allowing us to identify and determine concentrations of chiral solutions by the rotation measurement. The specific rotation value also depends on temperature and wavelength. When rotation is measured as a function of the wavelength, $\alpha = \alpha(\lambda)$, it is then the optical rotatory dispersion (ORD) technique.

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Many optically active substances such as sugar-water solutions possess light absorbing bands in the UV-spectral range and in the visible spectral range they are almost transparent. In some cases, optical measurements in the UV-range are challenging, making the use of the visible range more preferable. In such cases, the modified Drude's equation provides us with a suitable tool for ORD data analysis. The equation links together the optical rotation α and parameters k_1 and k_2 associated with molecular structure and concentration (in the case of a liquid solution) as follows:

$$\alpha(\lambda) = \frac{k_1}{k_2 + \lambda^2}. \tag{1}$$

When Eq. (1) is applied to a non-absorbing spectral range, the relationship between the optical rotation α and the right side (parameter side) of the equation is linear. It should be noted that the original Drude's equation also takes into account the wavelength of the absorption band of chiral molecules [3]. In practice, the absorption band located in a deep UV-spectral range can be difficult to determine.

Güçlü et al. [4] have shown results for sugar measurement based on data obtained from a commercialized ORD apparatus. They studied the properties of glucose, glutamine, and others at a selected spectral wavelength of 400–600 nm. From a calculation using a sample's concentration in a modified Drude's equation, they found a confirmation of concentration between calculation and actual concentration prepared. A fitting procedure has been used to improve the accuracy of optical rotation measurement. The work of Güçlü et al. is encouraging because the optical properties of some sugars that absorb light with peak absorbance in the UV region could be investigated although the performance of some commercial equipment in the UV spectrum is limited.

The ORD set-up consisting of a modulator between two perpendicularly oriented polarizers has been used to characterize a glucose sample for a diabetes mellitus disease investigation [5]. Such work was also conducted based on a glucose sensor by Ansari et al. [6]. The ORD set up was also introduced to measure sucrose by positioning the sample between the horizontally and vertically oriented polarizers and comparing the results to commercial ORD apparatus using the intensity and optical null measurement methods [7]. Such work indicated that the use of polarizers with a fixed polarization state in the ORD set-up is appropriate for liquid measurements.

The determination of the optical rotation of sugars (such as glucose, sucrose, sacarose, galactose, etc.) is appealing as these compounds exist in many industrial materials. The production of biofuels is growing rapidly along with new biorefinery plants [8]. In the processes of these plants, raw material obtained e.g. from wood, grass, and other biological waste is converted into ethanol which is further refined to make fuel. This process involves the breakdown of cellulose into several sugars [9]. Therefore, the developing biorefinery industry needs an appropriate apparatus to measure the concentration of often complex sugar solutions. Optical measurement such as ORD is one potential technique to meet the challenge describe above. By using an ORD technique the optical rotation of many sugar molecules with a chiral molecule structure can be determined with reasonable accuracy. The accurate characterization of material may lead to more efficient industrial processes and reduced emissions.

In this paper we report the results of optical rotation measurement applied to the modified Drude's equation for several sugar compounds such as glucose, xylose, arabinose, and galactose. In addition, the study includes samples of mixed sugar compounds. The use of the modified Drude's equation for this application can be considered unique. The measurement was done using a simple and self-constructed ORD set-up integrated with a commercial UV–vis spectrophotometer. Beside the optical rotation as a function of the wavelength, the set-up also provides a convenient way to conduct the reference measurement which is often crucially necessary in optical and spectroscopy experiments.

2. Materials and experiment

A diagram of the ORD apparatus used in this study is shown in Fig. 1. The set-up was constructed of a liquid sample/cuvette and two polarizers. The first linear polarizer was adjusted vertically (to 90°), meanwhile the second linear polarizer was adjusted to an angle of 45°. A liquid sample in a cuvette was placed in between the two polarizers. The set-up was integrated with the sample compartment of a commercial UV–vis spectrophotometer (Hitachi U-3300). The spectrophotometer used Tungsten-Halogen and Deuterium sources to produce a UV–vis light spectrum. The detector was a photomultiplier tube (PMT). The transmittance spectra of sugar solutions were scanned and stored for data-analysis.

The light transmittance through the set-up can be modeled using Jones calculus where polarized light is represented as a vector and the function of each optical component in a set-up can be expressed by a matrix. The matrix for a linear polarizer oriented at the angle of θ can be expressed as [1]:

$$T(\theta) = \begin{pmatrix} \cos(\theta)^2 & \cos(\theta)\sin(\theta) \\ \cos(\theta)\sin(\theta) & \sin(\theta)^2 \end{pmatrix}. \tag{2}$$

The sample (optically active material) changes the polarization state of the beam acting as a rotator and can be written as the Jones matrix below.

$$S(\alpha) = \begin{pmatrix} \cos(\alpha) & -\sin(\alpha) \\ \sin(\alpha) & \cos(\alpha) \end{pmatrix}, \tag{3}$$

where α is the optical rotation. Assuming that light emitting from the light source is linearly polarized at the angle of ϕ, the Jones vector for incident light can be expressed as:

$$J_{in}(\phi) = \begin{pmatrix} \cos(\phi) \\ \sin(\phi) \end{pmatrix}. \tag{4}$$

Based on these matrices and the orientation of the components, the output of the set-up J_{out} is

$$J_{out}(\alpha) = T(\theta + 45) \cdot S(\alpha) \cdot T(\theta) \cdot J_{in}(\phi). \tag{5}$$

As can be seen, the Jones vector for the output is a multiplication of all components involved in a set-up. The light intensity received by the detector is proportional to the square of J_{out} and depends naturally on the optical rotation value (and is practically linear when the rotation is less than a few degrees).

Using the original Drude's equation, the optical rotation, α_o can be calculated as below [1].

$$\alpha_o = \frac{K}{\lambda - \lambda_o^2}, \tag{6}$$

where K is a constant and λ_o is the absorption wavelength. To use this equation, the absorption wavelength must be known or determined. Unfortunately, for some materials this parameter is difficult to obtain. In such a case, use of the modified Drude's equation as expressed in Eq. (1) is preferable. For solutions, the optical rotation
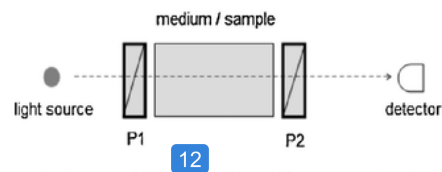

Fig. 1. Schematic diagram of ORD set up. P1 and P2 are denoted as linear polarizers.

α is linearly dependent on the concentration C and the thickness l of the sample. The relationship is as below [4].

$$\alpha = [\alpha]Cl. \tag{7}$$

The total optical rotation is the sum of accumulated molecular optical rotation within the solution.

Sugar compound 8 of alpha-D(+)-glucose (99+%, anhydrous, Acros Organics), D(+)-xylose (99+%, Sigma–Aldrich), L-(+)-Arabinose (>99%, Sigma–Aldrich), and D-(+)-galactose (98%, anhydrous, Sigma–Aldrich) were used for the measurement. Each sugar was dissolved in pure water for further characterization. First we used spectrophotometry to observe the locations of optical absorption bands over a UV-visible spectrum through 1 cm sample thickness. Secondly, we used the ORD set-up to obtain the transmission spectra of individual and mixed sugar solutions. The sugar sample was put in a 5-cm quartz cuvette corresponding to the light propagation path length. Both the absorption and ORD measurements and the material preparation were conducted at room temperature.

Optical measurements are usually relative *i.e.* data from the sample to be studied is compared to data obtained from a reference, well-known material. The ORD-measurement used in this study is also a relative technique, but it does not require a separate reference sample. By relocating the polarizer P2 in Fig. 1, the sample to be studied can be considered as a reference sample. For the reference measurement, the P2 is moved to the space between the P1 and the liquid/cuvette.

3. Results and discussion

Absorbance measurements of glucose, xylose, arabinose, and galactose dissolved in pure water were conducted using the spectrophotometer for a concentration of 30 g/L (using a 1 cm quartz cuvette) and the results are shown in Fig. 2. It was observed that absorbance for sugars occur at a UV-region of 220–290 nm. Although the absorption bands are not sharp in shape, distinguishable wavelengths associated to the bands for each sugar can be defined. Absorption peaks for glucose, xylose, arabinose, and galactose are observed at a wavelength of *ca.* 235 nm, 230 and 278 nm, 275 nm, and 290 nm, respectively. No absorption bands were observed for the sugars in a visible spectrum range.

As mentioned earlier, it can be difficult to determine optical rotation when the ORD technique is used in the UV-spectral range. Therefore, the ORD measurements were mainly carried out in the visible spectral range, from 300 to 800 nm. First we observed the light transmissions for a reference configuration (P1-P2-S) and secondly, the transmission for a measurement configuration (P1-S-P2). An example of transmittances is shown in Fig. 3a. The ratio of the
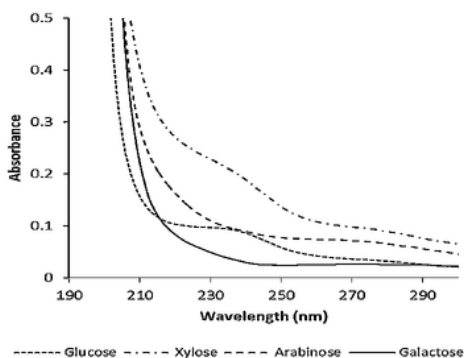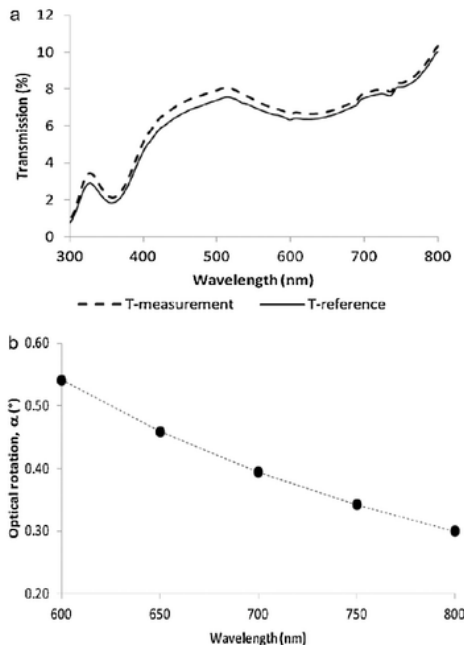

Fig. 3. (a) Light transmission of a sugar solution obtained from the measurement and the reference configuration. (b) Relationship between wavelength and optical rotaton for a glucose sample.
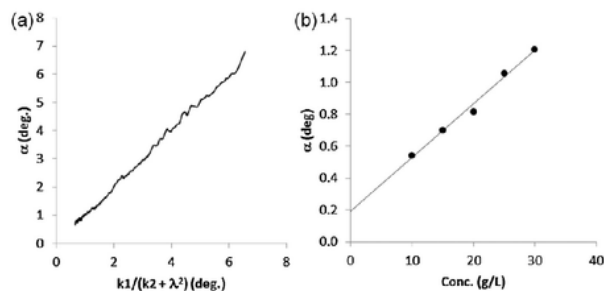

Fig. 4. Relationship between optical rotation α at 600 nm and (a) Drude's parameters and (b) concentration of glucose.

measurement and reference transmissions was calculated and by utilizing the Eq. (5) the relationship between the optical rotation and the wavelength was obtained. Such a relationship for a glucose sample (10 g/L) is shown in Fig. 3b.

By considering the Drude's parameters k_1 and k_2 as adjustable parameters, the theoretical optical rotation and experimental one may coincide. An example of such fitting is shown in Fig. 4a. A strong linear relationship between the experiment and calculation is found and the curve gradient was almost a unity. This fact can be used to indicate if there is something interfering with the measurements – when gradient values differ extensively, the measurement value should be rejected. It should be noted that in the UV region, absorption will cause nonlinearity to the curve. In such a case the ORD measurement can be used but with the original Drude's equation or using another form of data-analysis.

To confirm the accuracy of the ORD/Drude method, the test was carried out using sugar solutions of various concentrations. The test demonstrated a linear relationship between real sugar concentration and the optical rotation. The result for glucose is given in Fig. 4b.

Fig. 2. Absorbance spectra for various sugars (concentration of 30 g/L).

Table 1
Optical rotations and Drude parameters of sugars observed from the measurement at the wavelengths of 600, 700 and 800 nm.

Sugar	k_1 (mdeg μm²)	k_2 (μm²)	α (°)		
			600 nm	700 nm	800 nm
Glucose	0.478	−0.016	1.389	1.008	0.766
Xylose	0.151	−0.028	0.455	0.327	0.247
Arabinose	0.908	−0.013	2.616	1.904	1.448
Galactose	0.745	−0.007	2.112	1.543	1.177
Glucose + xylose	0.323	−0.017	0.943	0.684	0.519
			0.908 (ave)	0.656 (ave)	0.497 (ave)
Glucose + xylose + arabinose	0.515	−0.015	1.491	1.083	0.823
			1.465 (ave)	1.063 (ave)	0.807 (ave)
Glucose + xylose + arabinose + galactose	0.579	−0.005	1.633	1.195	0.913
			1.574 (ave)	1.142 (ave)	0.867 (ave)
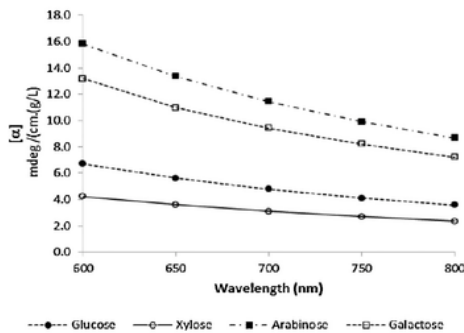
Fig. 5. Specific rotations for several sugars at various wavelengths from 600 to 800 nm.

Other sugar samples showed similar linearity. The offset value of α existing in Fig. 4b was taken into account in the calculation.

Fig. 5 shows the wavelength dependence of the specific optical rotation [α] for four sugar solutions. The curves are logical as the decrease of [α] is followed by an increase in wavelength for all sugar samples. Among the sugar samples, arabinose shows the highest value of [α] and the values decrease for the subsequent sugars, galactose, glucose, and xylose, respectively. The measurement results obtained for the specific optical rotation for glucose at 600 nm resembles the results obtained by Baba et al. [10]. However, their study concerned eye glucose monitoring using a different measuring technique.

Measurements were also conducted to investigate mixed sugars. The results (along with individual sugars) obtained from these tests are tabulated in Table 1 for the different wavelengths of 600, 700 and 800 nm. For the sample consisting of four sugars of the same concentration, the observed total optical rotation α_{TOT} was the average value of individual optical rotation expressed as:

$$\alpha_{TOT} = \frac{(\alpha_{gluc} + \alpha_{xyl} + \alpha_{ara} + \alpha_{glct})}{4}. \tag{8}$$

where α_{glu}, α_{xyl}, α_{ara}, and α_{glct} are the optical rotations of glucose, xylose, arabinose, and galactose, respectively.

As we can see from Table 1, optical rotation for individual sugar and mixed sugar shows good agreement between the result obtained from the measurement and calculation by taking the average value (notated 'ave'). Drude's parameters (k_1 and k_2) obtained from the fitting are also given. The proposed optical rotation model for mixed sugar molecules is considered valid by assuming that there is no molecular interaction among the sugars. Interaction could alter their molecular structure leading to a change in the optical rotation value. The experiment showed that the individual optical rotation of sugar contributes to the total value of optical rotation but not the summation as found for other sugar compounds as reported by Güçlü et al. [4]. The experiment has also shown that the proposed model is valid for mixed individual sugars with positive optical rotations and this phenomenon has not often been considered in other research. The optical rotation model for mixed sugars proposed in this work is encouraging as it could be applied to bio-refinery solutions consisting of sugars [8]. Further study could be initialized using the above results and the ORD set-up of this study for the identification of molecules.

4. Conclusions

By using the modified Drude's equation with the ORD polarization technique the optical rotation of sugar compounds (glucose, xylose, arabinose, and galactose) have been determined. This study has shown that the modified Drude's equation is valid for use with optically active material (such as sugars) providing that the absorption bands of such material do not exist in the wavelength range used in the experiments. Using the specific optical rotation, sugar sample concentration was calculated and confirmed with the concentration of the prepared sample. We proposed that the optical rotation model for mixed sugars should use the average of the optical rotation value of the individual sugars. This phenomenon can be used to deduce and analyze any solution of many sugars (such as bio-refinery solutions). The self-constructed ORD set-up offers a relatively simple and cheap tool that can be embedded into commercial spectrophotometers.

References

[1] E. Collett, Polarized Light: Fundamentals and Applications, Marcel Dekker, Inc., New York, 1993.
[2] J. Michl, E.W. Thulstrup, Spectroscopy with Polarized Light, VCH Publisher, Inc., New York, 1986.
[3] A.B. Shipovskaya, V.I. Fomina, D.A. Rudenko, S.Yu. Shchyogolev, Influence of physical and chemical modification on the optical rotatory dispersion and biological activity of chitosan films, Int. J. Polym. Sci. 2013 (2013) 1–6.
[4] B. Güçlü, G.A. Engbretson, S.J. Bolanowski, Constrained optimization of Drude's equations eliminates effects of confounding molecules for the polarimetric measurement of glucose, J. Biomed. Opt. 9 (5) (2004) 967–977.
[5] R.J. McNichols, G.L. Coté, Optical glucose sensing in biological fluids: an overview, J. Biomed. Opt. 5 (1) (2000) 5–16.
[6] R.R. Ansari, S. Böckle, L. Rovati, New optical scheme for a polarimetric-based glucose sensor, J. Biomed. Opt. 9 (1) (2004) 103–115.
[7] E. Castiglioni, S. Abbate, G. Longhi, Experimental methods for measuring optical rotatory dispersion: survey and outlook, Chirality 23 (2011) 711–716.
[8] B. Kamm, M. Kamm, Principles of biorefineries, Appl. Microbiol. Biotechnol. 64 (2004) 137–145.
[9] C.A. Cardona, Ó.J. Sánchez, Fuel ethanol production: process design trends and integration opportunities, Bioresour. Technol. 98 (2007) 2415–2457.
[10] J.S. Baba, B.D. Cameron, S. Theru, G.L. Coté, Effect of temperature, pH, and corneal birefringence on polarimetric glucose monitoring in the eye, J. Biomed. Opt. 7 (3) (2002) 321–328.

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8 use of N,N′-diallylaldardiamides as cross-linkers in xylan derivatives-based hydrogels", Carbohydrate Research, 2011
Crossref

9 words — < 1%

9 Egidio Giorgio, Rosario G. Viglione, Riccardo Zanasi, Carlo Rosini. "Ab Initio Calculation of Optical Rotatory Dispersion (ORD) Curves: A Simple and Reliable Approach to the Assignment of the Molecular Absolute Configuration", Journal of the American Chemical Society, 2004
Crossref

9 words — < 1%

10 www.epjap.org
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11 Fang Wang, Hui-Jing Wei, Yu-Fang Liu. "A fiber link equipment for the optical rotation measuring based on AC-DC modulation magneto-optical effect", Sensors and Actuators A: Physical, 2016
Crossref

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