Measurements and uncertainty budget for chiral liquids optical rotation at 633 nm

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Abstract. Here is presented the assembling of an extension of the polarimeter for optical rotation measurements in chiral liquids at 633 nm and 1 cm optical path. It was tested using a standard sucrose solution, and by comparison considering the assessed uncertainties on both the calculated expected and the experimental values. The normalized error criterion showed a very good agreement, and some discrepancies are possibly due to the cuvette material variation.

1. Introduction
Optical polarization of light was discovered in 1808 by Étienne-Louis Malus and has evolved into one main field of study [1]. One practical application is the study of the optical rotation of substances and its use in metrology. Quartz control plates (QCP) having their optical rotation well determined are standards used to calibrate polarimeters [2]. The Optical Metrology Division of Inmetro assembled a reference polarimeter for QCP calibration service [3, 4]. In order to extend the capabilities of the instrument for the measurements of chiral liquids, a device was designed and built in order to support and thermalize optical cuvettes. Optical rotation measurements in a solution of sucrose reference material were realized and the results were compared to the calculated expected values [2] considering the uncertainties on both measured and calculated values. Here we report on the first results from this system for the measurement of optical rotation at 633 nm of small amounts of chiral liquids [5].

2. Experimental set-up

2.1. The thermalization device
The optical rotation of a substance depends on its temperature and on the wavelength of the incident radiation, optical path and concentration. Temperature control is achieved by a circulating thermal bath through the polarimeter chambers, monitored by inserted thermistors. A developed device, based on a tested prototype [6], was assembled at the polarimeter, as shown in Figure 1: (a) the topped inserted cuvette (white lid visible), the inserted thermistor for the cuvette temperature control, and the air temperature measurement, near the device; (b) filled cuvette.

2.2. The preparation of the standard solution
In order to verify the accuracy of measurement in the modified polarimeter, a standard sucrose solution was prepared at the Electrochemistry Laboratory of Inmetro following ICUMSA [2]: 26.0160 g of pure sucrose dissolved in pure water to a final volume of 100.000 cm$^3$ under normal conditions.
The analytical balance was calibrated; Type I water was used to dissolve the commercial sucrose reference material of 99.5 % purity. The sucrose was slowly poured in a beaker and weighed, water added to the final desired weight and a magnetic agitator further homogenized the solution. Four clean and identified cuvettes of 1 cm optical path and 3.5 mL volume (as in Figure 1b) were filled and immediately taken to the Laboratory of Optical Applications (Laopt) for the polarimetric measurements. Four months later, the standard solution was prepared again and the measurements repeated.

2.3. The optical rotation measurements
The polarimeter has been described elsewhere [3, 4, 5]. It has two thermalized chambers: one contains a standard QCP for the polarimeter verification, and the other (Figure 1a) has the device with the cuvette. The whole instrument is automated with LabVIEW programs that also acquire, register and analyze data giving the mean values of the optical rotation and temperature. Each register consists of six repetitions of the measurement of the angle of rotation of the polarization plane of the radiation from a calibrated He-Ne laser of (632.990978 ± 0.000027) nm, from the QCP and sucrose solution; the temperature is controlled by the thermal circulating bath set at 20 °C, and is sensed by a calibrated thermistor inserted near the cuvette and registered during the acquisition. The four cuvettes were measured in the same day, delay time between them only due to optical alignment and temperature stabilization.

3. Experimental set-up
The measured optical rotation values were compared to the calculated expected values by the equations given in the ICUMSA standard [2] where the input parameters are the measured mass fraction and the temperature, and thus uncertainties were evaluated for the standard sucrose solution expected value. The polarimeter had already been characterized [4] and a new uncertainty budget was obtained for the modified setup [5]. The uncertainty analysis calculation was realized in an Excel worksheet.

3.1. Uncertainty evaluation of the measured mass fraction
The mass fraction, \( w \), was calculated from the mass values measured during the preparation, corrected by the balance calibration certificate and purity of the sucrose reference material. In (1) \( m \) is the corrected sucrose weighed mass, \( M \) is the corrected sucrose plus water weighed masses, and \( p \) is purity.

\[
\frac{w}{%} = \frac{m \times p}{M \times 100}
\]  

The uncertainty evaluation:
values of the optical rotation of standard sucrose solutions prepared on two distinct occasions on July, 27, 2016 (2a) and on November, 11, 2016 (2b) for the four identified cuvettes. The rotation in 546 nm is:

\[ u_w^2 = \frac{p^2}{(100 \times M)^2} \times (u_m)^2 + \frac{m^2}{(100 \times M)^2} \times (u_p)^2 + \frac{m^2 \times p^2}{(100 \times M)^2} \times (u_M)^2 \]  

where \( u_m \), \( u_M \) and \( u_p \) are the contributions due to \( m \), \( M \) and \( p \).

3.2. Uncertainty evaluation of the calculated optical rotation value

The ICUMSA equation in (3) establishes the value of the optical rotation, \( \alpha \), of a standard sucrose solution under the radiation of 546.2271 nm, for an optical path of 20 cm, as a function of the mass fraction (valid from 0 to 0.6), and at the temperature interval 18 °C to 30 °C:

\[ \alpha_{546} = a_01 \times w + a_{02} \times w^2 + a_{03} \times w^{23} + a_{04} \times w^4 + a_{05} \times w^5 + (a_{11} \times w + a_{12} \times w^2 + a_{13} \times w^3)(t - 20.005) \]  

where \( w \) is the mass fraction, \( t \) is the measured temperature, and the \( a_i \) are given constants. For notation simplicity the wavelengths values are depicted as 546 nm and 633 nm.

In order to compare with the measurements, the calculated value needs to be converted to the wavelength used at the polarimeter using the ICUMSA equation, where \( \lambda = 0.633 \mu \text{m} \), and \( a, b, c \) and \( d \) are given constants:

\[ \alpha_\lambda = \frac{a_{0,546}}{(a+b \lambda^2+c \lambda^4+d \lambda^6)} \]  

The temperature and mass fraction dependences of the optical rotation are independent in the validity range of the equation [2]. For the uncertainty evaluation in the calculated optical rotation, it was applied the Kratgen method, considering variations of the magnitude of the uncertainties in \( w \) and in \( t \). For a fixed \( t \), the difference in calculated (3) for \( w \) and \( w + u_w \) resulted in the contribution to the optical rotation uncertainty due to the uncertainty in the mass fraction, \( u_{aw}^2 \). Considering a fixed \( w \), (3) was calculated for \( t \) and \( t + u_t \), resulting the contribution to the optical rotation uncertainty from the uncertainty in the measured temperature \( u_{at}^2 \). The resulting uncertainty in the calculated optical rotation in 546 nm is:

\[ u_{a,546}^2 = u_{aw}^2 + u_{at}^2 \]  

The uncertainty in the calculated optical rotation in 633 nm was obtained by applying (4).

3.3. Uncertainty evaluation of the measured optical rotation value

The influence factors were studied and the main components for the uncertainty evaluation come from the traceability of the standards, type B, normal, the optical alignment, type A, normal, acquisition and analysis methods considered under the repeatability, type A, normal. As a numerical example, the components \( c_i \) already in units for optical rotation measurements are: \( c_1 \) from the laser wavelength calibration certificate, \((2.97 \times 10^{-6})^2 \); \( c_t \) from the QCP calibration, 0.0005°; \( c_{\text{temp}} \) for the temperature sensor calibration, \((3.15 \times 10^{-5})^2 \); \( c_{\text{axis}} \) from the optical axis of the polarimeter, 0.0004°; \( c_{\text{rep}} \) from the repeatability, 0.0002°. Following the GUM [7], it was calculated the effective degrees of freedom, the standard combined uncertainty \( U_c = 0.0005° \), and the coverage factor, \( k = 2.00 \), resulting the expanded uncertainty \( U = 0.001° \).

4. Results and Discussion

In order to do the comparison with the calculated values the measured values and uncertainties were multiplied by 20, as the optical path in the cuvette is 1 cm and the equation (3) is for a 20 cm optical path. The mass fraction values and uncertainties of the first preparation was \( w_1 = 0.25882 \pm 0.00026 \) and for the second was \( w_2 = 0.25879 \pm 0.00026 \). Figure 2 shows the calculated (squares) and measured (circles) values of the optical rotation of standard sucrose solutions prepared on two distinct occasions on July, 27, 2016 (2a) and on November, 11, 2016 (2b) for the four identified cuvettes. The uncertainties were plotted as error bars in the graphs.
Figure 2. Calculated (squares) and measured (circles) optical rotation values of sucrose solution: (a) on July, 27, 2016 and (b) on November, 11, 2016.

The calculated values are practically constant in each day and very repeatable, their averages and standard deviations are $(32.7829 \pm 0.0002)^\circ$ and $(32.7781 \pm 0.0002)^\circ$. Those values although very precise still do not present the necessary reliability for the comparison, what was achieved with the uncertainty assessment which values are presented on table 1. The measured values are more spread, and in the second day one was considered outlier. The cuvette quality appears to be the driving factor of the discrepancies and a systematic study is a future improvement.

The acceptance criterion for the comparison was the normalized error $E_n < 1$ taken between the calculated and measured averaged values and respective uncertainties, presented in Table 1. The obtained $E_n$ values were very small even considering the outlier, 0.0013 for the first day and 0 or 0.0019 for the second, attesting the good performance of the modified polarimeter for optical rotation measurements on chiral liquids under 633 nm radiation.

**Table 1.** Average optical rotation values and uncertainties of a standard sucrose solution under radiation of 633 nm, at 20 °C and 20 cm optical path.

| Date           | Calculated, $U$ | Measured, $U$ | $E_n$  |
|----------------|-----------------|---------------|--------|
| July, 27       | 32.78° 0.04°    | 32.84° 0.02°  | 0.0013 |
| November, 11   | 32.78° 0.04°    | 32.78° 0.02°  | 0      |
| outlier        | 32.69° 0.02°    | 0              | 0.0019 |
5. Conclusions
Here is presented the assembling and first measurements of an expansion of the reference polarimeter of Laopt for the measurements of the optical rotation of chiral liquids under 633 nm and 1 cm optical path. The system was tested with a standard solution of a commercial sucrose RM for which the calculated expected values of the optical rotation were compared to the measured ones taking into account the uncertainties. The agreement was good and pointed to improvements in the system, and to the use of a purest reference material. A new result brought by this work was the assessment of the uncertainty on the calculated expected value.

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