Development of holmium oxide glass calibration system measured using mathematical modelling

Y Prihapso¹, A Achmadi¹, D Suryani¹, W Farhania¹, Nelfyenny¹ and H Zaini¹

¹Sub-directorate of National Measurement Standards for Photometry and Radiometry (SNSU), National Standardization Agency of Indonesia (BSN), Serpong, Banten, Indonesia

E-mail: yonan@bsn.go.id

Abstract. Holmium oxide glass filter has known to exhibit persistence absorption lines across the visible region. Due to these properties, a holmium oxide glass filter is used as a reference standard to calibrate the wavelength accuracy of a spectrophotometer. In this research, a system consists of a double-monochromator and a photomultiplier tube will be evaluated. Mathematical modelling is used to calculate the true value of the absorption lines of the holmium glass filter to compensate for the low optical resolution of the double-monochromator system. Measurement results are validated by comparison with the single-monochromator-order shorting filter system which has higher optical resolving power. Wavelength differences between double-monochromator and single-monochromator systems are better than 0.1% and within the expanded uncertainty of 0.32 nm. Therefore, the double-monochromator system is suitable to provide measurement traceability for the calibration of holmium oxide glass filters.

1. Introduction

Spectrophotometer has been widely used in science and technology research to measure quantitatively interaction of materials and radiation. One of the properties of light and material interaction that commonly used is the absorption of photons. This interaction is used in the chemical analysis where photon absorption relates to the volume, purity, or the size of materials being measured [1]. This information is important mostly in the pharmaceutical industry, food, or even in environmental management. As an assurance of stability and measurement accuracy, especially in pharmaceutical products, this instrument needs to be validated and calibrated regularly.

Several methods are described in ASTM E 275 [2] and ASTM E925 [3] to provide evidence of acceptable analytical measurement results of a spectrophotometer. Holmium oxide glass is commonly used in the measurement of wavelength accuracy of a spectrophotometer [4]. Holmium oxide is known to exhibit strong absorption lines in the visible spectral range [5, 6]. The glass type instead of the solution is widely used as a reference due to its stability over long time periods, compact size, and relatively easy to use. This reference also does not induce error due to slit function that occurs when atomic emission lamps are used. The latter property is advantageous, especially since spectrophotometers that widely used in Indonesia have spectral bandwidth (SBW) ≤ 2.0 nm, which erroneous when used to measure atomic lines.

In this research, a system composed of a double-monochromator with low response time, low noise, and high gain photomultiplier tube designed to calibrate holmium oxide glass. The double monochromator aligned in the additive mode which reduces the stray light, especially heterochromatic
stray light [7]. Thus, provide a high signal-to-noise ratio in the lower spectral range where the radiation is low. To improve the spectral resolving accuracy of the system, a mathematical model based on Caruana’s algorithm is used. This algorithm provides less tedious algebra with high accuracy since this algorithm is unaffected by the noise exist in the spectral data [8, 9]. Based on tolerance limit set by pharmacopeia in the UV range, the tolerance limit is 1.0 nm and in the visible range, 3.0 nm [10]. In this research, it is expected that the peak estimation for holmium oxide glass would be within the tolerance limit of 1.0 nm at UV and visible spectral range.

2. Method

The system developed consists of a double monochromator, a photomultiplier tube (PMT), and data acquisition hardware connected to a computer for analyzing the measurement results. The double-monochromator is an AMKO LTI made up of two monochromators aligned together in the additive mode mounted on a common base plate. The monochromator optical components are aligned based on the Czerny-Turner with the first monochromator exit slit and second monochromator entrance slit are connected together as shown in figure 1 (a).

A 250 W tungsten halogen lamp is used as the light source operated in a stabilized DC supply. The detector is a photomultiplier tube (PMT) from Hamamatsu with an 8 mm round window having a peak sensitivity at 400 nm. The detector dynamic range is up to \(10^9\) where its output is feed into an ADC (analog to digital converter) which read the monochromatic beam intensity correspond to wavelength position as shown in figure 1 (b). The wavelength position acquired from the signal at the analog output of the double monochromator driver. As shown in the schematic, the monochromator driver starts/stop button will trigger 5-phase motor driver which control the movement of the mechanical grating of the first and second monochromator synchronously. During the movement, every 0.2 nm step a 5-volt pulse signal is generated at the analog output. In the case of a double-monochromator scanning range equals to 180 nm, there will be around 900 pulses generated. Therefore, by recording these pulses at analog out, the wavelength position of double monochromator can be determined.

3. Results and Discussion

The mechanical resolution of the double-monochromator movement is known to be 0.2 nm therefore the spectral bandwidth of the measurement system cannot lower than this value. The first monochromator grating is ruled with a groove number of 1200 l/mm blazed at 400 nm and the second grating 600 l/mm blazed at 1250 nm. The reciprocal linear dispersion of the first monochromator is 4 nm/mm and the second monochromator is 8 nm/mm. Due to additive alignment mode, the dispersed beam from the first monochromator is dispersed further by the second monochromator [11], therefore the final dispersion of the double monochromator is equal to 4 nm/mm. The mechanical slit width can be adjusted from 0 to 1.0 mm with an incremental step of 2.0 μm, therefore the spectral bandwidth (SBW) of the double monochromator can be calculated with equation 1.
Where, $SBW$ is the spectral bandwidth of double monochromator in nm, $D$ is the dispersion of a 1200 l/mm grating in nm/mm, $S$ is the slit width in mm, and $l$ is the number of groove line of the grating used in the double monochromator. The theoretical minimum $SBW$ of the double monochromator is 0.08 nm and the maximum is 4.0 nm. Due to the limitation of grating mechanical movement, the minimum $SBW$ can be achieved is equals to the mechanical movement resolution.

$$SBW = \frac{1200 \cdot D \cdot S}{l}$$  \hspace{2cm} (1)

Figure 2. Signal acquired from double monochromator driver analog out and photomultiplier tube detector.

The analog signal of the monochromator grating movement recorded synchronously with the voltage output of the PMT which corresponds to the monochromatic beam intensity at the exit slit of the double-monochromator. The recorded signal is shown in Figure 2, grating movement is marked by the rising edge of the signal pulse at the analog out. The stop sign can be calculated from the scanning range of the double monochromator. For example, in the scanning range of 180 nm, the pulse generated at the analog out is 900 pulses and the stop sign of data recording is at 900th pulse.

Holmium oxide glass spectral responsivity is measured for band 6th, 7th, 8th, 9th, and 10th in the spectral region from 380-560 nm. These bands consist of a broadened peak and a sharp peak that suitable to test the spectral resolving power of the double monochromator system compared to the mathematical modelling analysis. These bands also located at the lower spectral region where the radiation intensity provided by the 250 W tungsten halogen is low. Thus, this region is susceptible to noise and stray lights that cause erroneous of the true absorption peak measurement. Holmium oxide glass spectrum profile is measured in transmittance quantity, to estimate absorption peak this value needs to be converted into absorbance quantity using equation 2.

$$T_H(\lambda) = \frac{T_c}{T_0}$$

$$Abs_H(\lambda) = \log \left( \frac{1}{T_H} \right)$$  \hspace{2cm} (2)

Where $T_H$ is the holmium oxide spectral profile, $T_0$ is the blank measurement without the holmium oxide glass placed in the cuvette, $T_c$ is curve measurement where the holmium oxide glass is placed in the cuvette, and $Abs_H$ is the absorbance spectral profile of the holmium oxide glass. Measurement results are shown in Figure 3, for the blank profile, curve profile, transmittance, and the correlated
absorbance profile of the holmium glass. Using the absorbance profile, the absorption peak of holmium oxide can be estimated by means of maximum height at the band regions.

![Absorbance Profile](image)

**Figure 3.** Measurement result of holmium glass for: (a) $T_0$-measurement without holmium glass, (b) $T_{H}$-measurement with holmium glass, (c) $T_{ir}$-transmittance profile, (d) $Abs_{ir}$-absorbance profile.

### 3.1. Mathematical Model for Peak Estimation

The Gaussian function is known to represent distribution with a symmetrical bell-shape around its center. The mathematical form of the Gaussian function is shown in equation 3, where this function controlled by three parameters $A$, $\mu$, and $\sigma$.

$$y(x) = Ae^{-\frac{(x-\mu)^2}{2\sigma^2}}$$  \hspace{1cm} (3)

Where, $A$ corresponds to the magnitude of the curve, $\mu$ corresponds to the position of the center location of the curve, and $\sigma$ corresponds to the width of the curve along in the $x$-axis. In spectroscopy, this curve can be used to fit the absorption curve of photon-material interaction. The absorption peak is then can be determined efficiently from the $\mu$ parameter in the Gaussian function. To solve the fit model an approach by transforming the non-linear function into amenable polynomial fit is used. The Caruana’s algorithm taking the natural logarithmic (ln) of the data to solve the mathematical model into linear second-order polynomial as shown in equation 4.
Figure 4. Determination of Gaussian parameters by parabola fit (lines) to the logarithmic value of observed data (dotted) for determining holmium glass peak position at (a) band 6th, (b) band 7th, (c) band 8th, (d) band 9th, and (e) band 10th.
By using parabola curve fit in the least square method, coefficient $a$, $b$, and $c$ are determined, thus the Gaussian parameters may be obtained as in equation 5. The fit results for band $6^{th}$, $7^{th}$, $8^{th}$, $9^{th}$, and $10^{th}$ of holmium oxide glass absorption profile are shown in Figure 4.

$$
\sigma = \frac{1}{(-2c)^{1/2}}
$$

$$
\mu = \frac{-2c}{\sqrt{\frac{a-b^2}{4c}}}
$$

$$
A = Ae^{\frac{x^2-2\mu x+\mu^2}{2\sigma^2}}
$$

$$
= \ln \left( A e^{\frac{x^2-2\mu x+\mu^2}{2\sigma^2}} \right)
= \ln \left( \frac{A}{e^{\frac{x^2-2\mu x+\mu^2}{2\sigma^2}}} \right)
= \ln \left( \frac{A}{e^{\frac{2\mu x - \mu^2}{2\sigma^2}}} \right)
= \ln(A) - \frac{\mu^2}{2\sigma^2} + \frac{2\mu x}{2\sigma^2} - \frac{x^2}{2\sigma^2}
= a + bx + cx^2
$$

The peak position result from using Caruana’s algorithm are shown in Table 1, where these results are compared to the peak position obtained by means of maximum height with double monochromator readings and also single monochromator which has a higher optical resolution.

3.2. Measurement Validation
Measurement results are validated against the single-monochromator with an optical resolution of 0.1 nm at a spectral bandwidth of 2.0 nm. The validation shows systematic error in the measurement of the holmium absorption peak using the double monochromator system. The systematic error appears as an increased or decreased value and affecting all the peak measurement results. Knowing this information prediction of the error magnitude at other wavelengths can be estimated and corrected.

| Absorption Band | Single Monochromator (nm) | Double Monochromator (nm) | Mathematical Model (nm) |
|-----------------|---------------------------|---------------------------|-------------------------|
| Band 6$^{th}$   | 418.67                    | 419.20                    | 419.14                  |
| Band 7$^{th}$   | 445.92                    | 446.20                    | 446.30                  |
| Band 8$^{th}$   | 453.78                    | 453.60                    | 453.69                  |
| Band 9$^{th}$   | 460.26                    | 460.20                    | 460.20                  |
| Band 10$^{th}$  | 536.43                    | 537.20                    | 537.15                  |

Holmium absorption peaks measured with single-monochromator are used as the reference value for the other two measurements as shown in table 1. The errors subtracted from this validation are used as
the correction for the systematic error that appears in the measurement. The mathematical fit model shows a closer peak estimation to the reference value.

Figure 5. Measurement error from double monochromator system compared with mathematical model.

The comparison peak measurement error using the double monochromator system alone with the mathematical fit model is shown in figure 5. The mathematical model shows a reduced error which increases the accuracy of the peak estimation. Using this information, a polynomial fit can be calculated to provide correction along the wavelength range for the double monochromator system.

Currently, there are more than 500 spectrophotometers throughout Indonesia that need to be calibrated each year. These instruments commonly have SBW ≤ 2.0 nm, therefore the holmium oxide glass is measured for its peak at this spectral bandwidth. Using the correction for the systematic errors in the double monochromator, the peaks of holmium oxide glass is estimated as presented in table 2.

An increase in the SBW as a function of slit width results in the broadening of the absorption peaks. This broadening effect can be clearly observed in peak estimation of the 7th, 8th, and 9th of the holmium oxide glass bands. These three bands are located close to each other, therefore due to increased SBW these peaks appear to be connected together as a single peak.

| Holmium Absorption Peak | Spectral Bandwidth (nm) |
|-------------------------|-------------------------|
|                         | 0.2         | 1.0         | 2.0         |
| Band 6th                | 418.67      | 417.66      | 415.44      |
| Band 7th                | 445.92      | NA          | NA          |
| Band 8th                | 453.78      | 456.42      | 452.98      |
| Band 9th                | 460.26      | NA          | NA          |
| Band 10th               | 536.43      | 537.04      | 538.68      |

3.3. Measurement Uncertainty Evaluation

Measurement uncertainty based on ISO GUM [12] is being used to estimate random errors that emerge from peak measurement using double-monochromator system. The measurement uncertainty associated with holmium glass absorption peak estimation is calculated based on the measurement equation in equation 2. The components constructing the uncertainty evaluation are from type A evaluation which can be estimated from repeated measurements. The other components are from type B evaluation that consists of uncertainty from the reference, spectral bandwidth, mechanical resolution, and fit error from the mathematical model.

Uncertainty evaluation associated with peak measurement at spectral bandwidth 0.2 nm shows that measurement results are in agreement within 1.0 nm tolerance limit as shown in figure 6. From this
result can be concluded that the double monochromator system together with applying Gaussian fit can be used to perform wavelength calibration of holmium oxide glass.

4. Conclusion
In this paper, the performance evaluation of the double monochromator system is presented. The demerit from mechanical resolution can be covered with a mathematical model which increases the accuracy of the peak estimation. Wavelength error at spectral bandwidth 0.2 nm is less than 0.1 %, with uncertainty associated with peak measurement of 0.32 nm. Thus, the double monochromator system is adequate to provide measurement traceability for holmium oxide glass at National Measurement Standards for Photometry and Radiometry (SNSU).

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