Stability study of standards used for calibration of the spectrophotometer wavelength scale

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Abstract. The calibration of spectrophotometers is a procedure recommended by international standards to provide quality assurance of results and traceability. Due to its intrinsic properties, holmium oxide filters are indicated as reference standards for calibrating the wavelength scale of such equipment. This paper presents a study aiming to assess the repeatability and drift of holmium oxide standard filters calibrated in the Radiometry and Photometry Laboratory (Laraf) of Inmetro in order to verify their stability.

1. Introduction

Spectroscopy is an analysis methodology studies the interaction between substances and electromagnetic radiation, through sophisticated optical instruments. This technique has been used in increasing proportions to quantify substances and to determine the concentrations because it is simple, fast and provides reliable results. It is widely used in the areas of water analysis, biology, physics, chemistry, and pharmaceuticals, in the polymer and petrochemical industry, among others.

All equipment used for tests and /or calibrations, which have significant effect on the accuracy or validity of the result must be calibrated and checked periodically in order to maintain traceability [1]. For these periodic checks and characterizations, there are international standards that determine the types of tests that must be made and that the reference should be used. The holmium oxide is one of the most recommended spectrophotometry filters for calibration of wavelength scale, because of its characteristic absorption peaks.

In studies developed by NIST (National Institute of Standards and Technology), holmium oxide standards were compared among national metrology institutes of several countries, all of them have control of environmental conditions and storage techniques and handling of filters. These studies show results obtained from analysis of the absorption bands of holmium oxide standards [2, 3, 4]. These standards have intrinsic characteristics and remained stable for many years. It is important to note that this stability is related only to the wavelength scale (abscissa) as the photometric scale (ordinate) may be subject to changes due to environmental conditions and contamination on the glass surface.

The Laboratory of Radiometry and Photometry (Laraf) at the Division of Optical Metrology (Diopt) of Inmetro has calibration services for optical filters used in the calibration of spectrophotometers.

Once the lab has measured a lot of wavelength standards, comparative studies of data will be made to verify the behavior of these standards between themselves, since they are from different manufacturers, used and handled in different ways. Such analysis will allow conclusions about the

holmium oxide behavior, since those standards analyzed were kept in unknown conditions which could influence the final result.

This paper describes the comparative analysis of the absorption bands values of different holmium oxide filters measured in Laraf.

2. Materials and methods

The spectrophotometer is an instrument used for measuring the amount of light absorbed or transmitted through a substance, whether solid, liquid or gas. With this technique, unknown components present in a sample can be identified, because their absorption bands are sensitive to ultraviolet, visible and infrared radiation.

The holmium oxide filter used as a reference standard to verify the wavelength scale can be found in two forms: liquid solution in cuvette cells and glass within a cuvette mount [5].

Although both filters are based on the same substance (holmium oxide), glass filters have near infrared region bands that are not present in the solution filters due to absorption by water. Consequently, the characteristic peaks values used are different in each case [3].

In the case of solution filters, when measured for a spectral bandwidth of 1 nm, characteristic peaks used for measurements at the spectrophotometric system were: (241; 250; 278; 287; 333; 345; 361; 386; 416; 451; 468; 485; 537; 641) nm, according to the articles published by NIST [2, 4] used as reference in the study, using the minimum presented uncertainty (0,2 nm).

For glass filters, the certified wavelengths of minimum transmittance for a spectral bandwidth of 1 nm are: (241; 279; 287; 333; 360; 385; 418; 453; 460; 536; 637) nm [3] with an uncertainty of 0,2 nm (k = 2). Some differences in the found peaks can be seen mainly in the band of 241 nm because some filters have an absorption variation in this region, depending on the base glass used.

In the measurements analyzed, it was used the scanning method, which there is a scan from the wavelength with greater value (initial) towards the lower value (final), presenting the peak values of the holmium oxide. This spectrum is exemplified in figure 1.

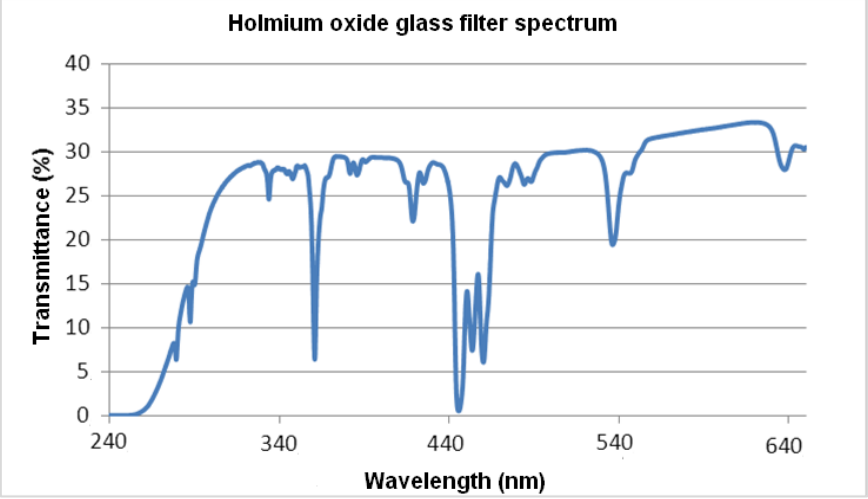

Figure 1. Holmium oxide glass filter spectrum.

The main parameter in the spectrum is the position of the found peaks, since the transmittance value can be considered irrelevant.

The analyzes were made using as base holmium oxide filters measured in the laboratory with the following specifications: analysis scale of 230 nm to 680 nm and scanning speed of 30 nm/min to 60 nm/min, being a total of 5 cycles or more with spectral bandwidths of 1 nm. The analysis was presented as percentage transmittance (%).

3. Results and discussions

In total, 90 measurements of holmium oxide filter data, among the years of 2000 and 2015 (between calibrations and recalibrations) were analyzed. Among the 90 holmium oxide filter measurements made by the laboratory in the midst of the years cited, 87 % of these measurements were made with glass filters doped with holmium oxide and 13 % with solution filters.

For holmium oxide solution filters, the results from 12 filters measurements were compared with each other (2001-2014 among calibration and recalibration). The peaks were compared with the values provided by NIST [2]. Errors are shown in the figure 2. It was used the lowest measurement uncertainty, provided by the NIST certificate, 0,16 nm, as the maximum and minimum limits of acceptance of the variation among the peak values provided by NIST and the measurement results.

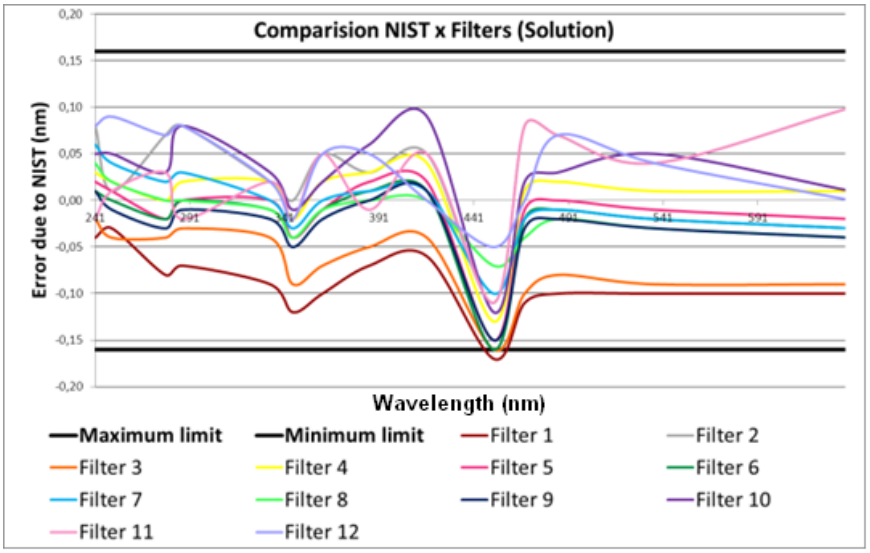

Figure 2. Comparison chart between the values provided by NIST for filters and Laraf measurements.

It is noted that only filters 1 (with an error of 0,17 nm), for the wavelength of 451 nm, ranged 6 % (0,01 nm) of the reference value.

Regarding holmium oxide glass filters, the values for the 78 glass filters measurements made in the laboratory (a total of 12 different manufacturers) from 2000 to 2015, between calibration and recalibration, were compared (figure 3).

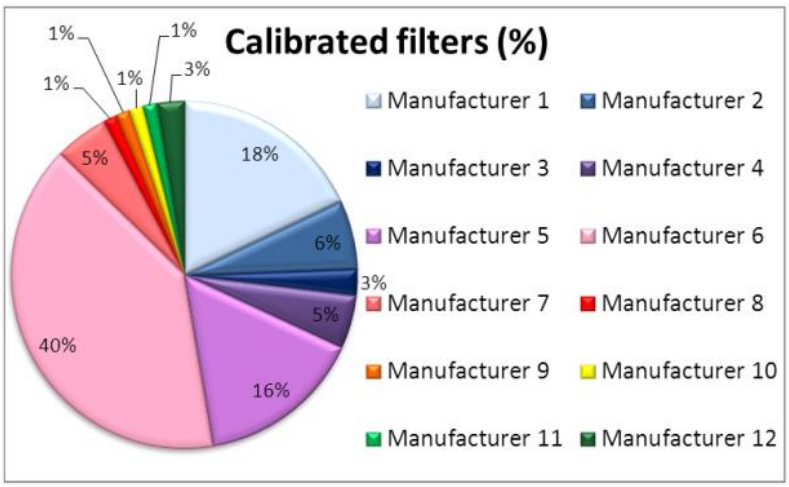

Figure 3. Ratio among manufacturers and filters calibrated in the laboratory, since 100 % is the total of 78 glass filters measurements.

As there was no data on the types of glass used in each measurement, it was adopted that filters provided by the same manufacturer had the same composition. For this reason, filters of the same manufacturer data were compared, getting an average of peaks by manufacturers.

The curves shown in the figure 4 represent the comparisons among such manufacturers and peak values supplied by NIST. It was used the measurement uncertainty of 0,20 nm as a parameter for the maximum and minimum limits of the analysis.

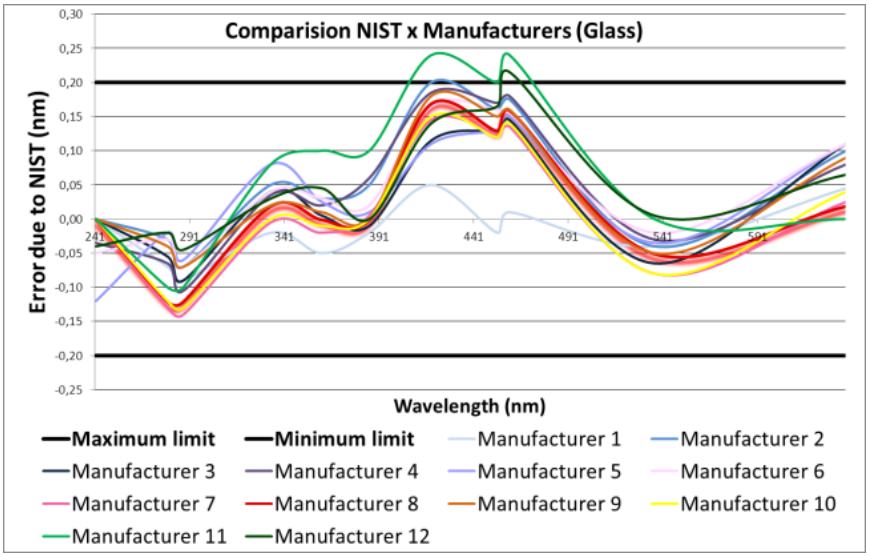

Figure 4. Comparison chart between manufacturers peak values (their mean) and the values provided by NIST onto glass filters.

The manufacturer 11 has a deviation of 20 % of the uncertainty value for the wavelength of 419 nm. This manufacturer also has a 20 % deviation for peak 460 nm, along with manufacturer 12, which deflects 10 % of the reference value. It is noteworthy that the manufacturer 11 is 1 % of the analyzed filters, equivalent to only a filter.

4. Conclusion

In this study it was observed through the figures 2 and 4, that there are variations in peak values for some filters and manufacturers. However, the vast majority of analysis filters (± 96 %) maintained their drift lower than the uncertainty provided by NIST of 0,16 nm and 0,2 nm, which is acceptable for holmium oxide filters when calibrated spectral bandwidth smaller than 2 nm. Based on the extensive study of holmium oxide standards, it can be seen that there is the need to make an initial calibration as soon after the acquisition of the standard, and periodic checks by the client comparing previous certificates or absorption bands values supplied with those measured in equipment. If the values found are not expected, it is recommended a recalibration.

It should be noted that holmium oxide standards should be used for verification of spectrophotometers wavelength scale in the UV/VIS region, it is not recommended its use in verification/calibration of a different scale.

To ensure the filters' highest integrity, it is recommended the proper use of the filter with gloves, storage free of dust and under controlled environmental conditions.

Acknowledgments
Thanks to Petrobras for the the financial support through the Programa Petrobras de Formação de Recursos Humanos (PFRH) and to the Curso Técnico em Metrologia from Inmetro.

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