

Metrological traceability of holmium oxide solution

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Abstract: Holmium oxide solution was prepared as a candidate of certified reference material for spectrophotometer wavelength scale calibration. Here is presented the necessary steps for evaluation of the uncertainty and the establishment of metrological traceability for the production of this material. Preliminary results from the first produced batch are shown.

Keywords: Certified reference material, holmium oxide, spectrophotometry, traceability, measurement uncertainty.

1. INTRODUCTION

According to ISO/IEC 17025[1], a measurement result is reliable when it presents evidence of its traceability, accompanied by an estimative of its measurement uncertainty. In measurements performed with UV/Vis spectrophotometry, these requirements can be fulfilled with the proper use of certified reference materials (CRMs).

1.1. Metrological traceability and CRM

Metrological traceability can be defined as the property of a measurement result related to a reference through an uninterrupted and documented chain of calibrations, contributing to measurement uncertainty [2]. Measurement uncertainty is a parameter associated with each measurand, adequate to the intended use of the measurement results [2]; it indicates data quality and helps interpretation and decisions taking.

CRMs are one of the main bases for attainment of accuracy and reliability of chemical measurements. Its use is a requirement for the process of equipment calibration and method validation. CRM definition in ISO 17034 [3]

states that the material must be characterized by a metrologically valid procedure (traceable to the International System of Units or to an internationally accepted scale) and it must be accompanied by a certificate that provides the property value, its associated uncertainty and a statement of metrological traceability.

1.2. Spectrophotometry

The spectrophotometry technique has low operational cost and is easy to use. Spectrophotometer is a fundamental instrument for analysis of several parameters in many areas, and thus, it is very important to verify its performance and also to keep the measurements traceability.

UV/Vis spectrophotometer measures the amount of absorbed light in ultraviolet (UV) and visible (Vis) spectrum by chemical compounds, allowing to quantify its concentration in different samples. Many analytes have their sensitivity intensely reduced due to a small variation in wavelength, and thus, calibration of the spectrophotometers wavelength scale is essential for measurements accuracy. CRMs are usually

employed for periodic verification and calibration of the equipment [4].

Holmium oxide CRM (Ho_2O_3) is the principal substance used as reference for the UV/Vis spectrometers and spectrophotometers wavelength scale calibration due to its stability and characteristics. It presents intrinsic and well resolved sharp peaks from 240 nm to 640 nm, covering the range used by the majority of the laboratories in diverse areas such as petrochemical and pharmacological. There are others CRMs with extended wavelength range into the infrared, but they are compounds into a glass matrix, which results in broader peaks and bands, and are less stable. The development of a CRM for spectrophotometers wavelength accuracy, such as Ho_2O_3 , is important to assure reliability of the measurements results made by the laboratories.

1.3. Objective

This work aims to present the methodology for establishment of metrological traceability and for calculating measurement uncertainty of produced Ho_2O_3 CRM used for the wavelength scale calibration of UV/Vis spectrophotometers. This type of CRM will be the first one developed in Brazil.

2. EXPERIMENTAL

2.1. Ho_2O_3 CRM production

The developed CRM was the Ho_2O_3 solution, which is essential to guarantee the reliability of UV/Vis spectrophotometric analysis.

The production was based on the procedure of Weidner *et al.* [5], with 99.99 % purity Ho_2O_3 and 70% perchloric acid (HClO_4). A 4 % Ho_2O_3 solution in 10 % HClO_4 was gravimetrically prepared. The acid solution was bottled into 5 mL ampoule of clear glass containing a volume of approximately 4 mL, as shown in figure 1. This procedure was accomplished at Inmetro's

Electrochemistry Laboratory.

In order to meet the ISO 17034 requirements [3], the homogeneity and stability of the produced batch must be assessed. These studies are ongoing. The batch characterization will be performed through a comparison between Inmetro's Radiometry and Photometry Laboratory and Visomes Laboratory, and further combination of the results.



Figure 1. Candidate CRM of Ho_2O_3

2.2. Traceability

Inmetro and Visomes spectrophotometers wavelength scale have been calibrated by using SRM-2034, a standard from the National Institute of Standards and Technology (NIST), in order to guarantee the measurements traceability in the Ho_2O_3 characterization. It was used for both the measurement method validation and the produced CRM batch traceability. The sources of uncertainty considered for the spectrophotometer calibration are showed in figure 2.

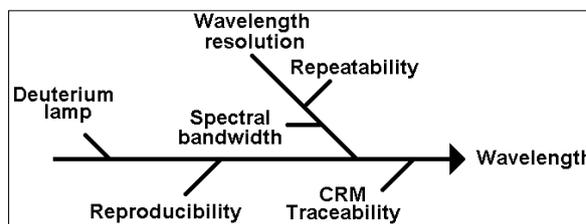


Figure 2. Ishikawa diagram with wavelength uncertainty sources for spectrophotometer calibration

The SRM-2034 has certified wavelength values of minimum transmittance for 14 bands

from 240 nm to 650 nm, for spectral bandwidth of 1 nm. The certified wavelengths are metrologically traceable to the SI derived unit expressed as nanometer.

2.3. Uncertainty evaluation

The uncertainty of the CRM produced will be evaluated according to the ISO GUM [6] and ISO GUIDE 35 [7]. For the CRM certified value, the following uncertainty contributions will be considered: (a) characterization, (b) non-homogeneity of the material, (c) changes in property values during transport (short-term stability), (d) changes in property values during storage (long-term stability).

3. RESULTS

After bottling the first batch, a sample of the CRM was measured and a spectra can be observed in figure 3. The spectrophotometer has dual beam, double monochromator, wavelength range from 190 nm to 900 nm. The parameters were: 0.01 nm resolution, 1 nm spectral bandwidth, 20 nm·min⁻¹ scanning speed, cycles of 2 measurement and 3 replicates, using a 10 mm optical path quartz cuvette.

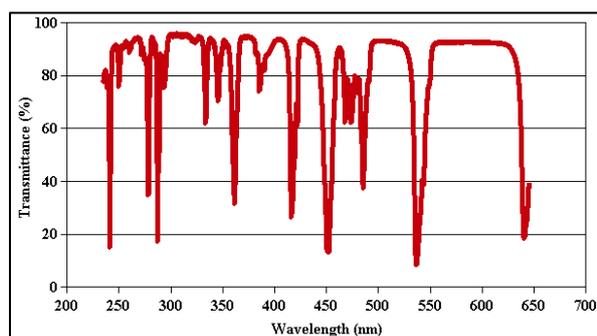


Figure 3. Absorption spectra of Ho₂O₃ in perchloric acid.

Table 1 shows the preliminary results of the measured sample together with the calculated normalized errors (En) between the SRM-2034 certified values and the produced Ho₂O₃ CRM candidate measured values. All of the 14 peaks ranging from 240 nm to 650 nm for spectral

bandwidth of 1 nm were employed. For all peaks resulted En<1, indicating satisfactory results. According to these preliminary results one can proceed to the studies for certification of the batch of the candidate CRM of Ho₂O₃.

Table 1. Comparison between SRM-2034 values and measured values from candidate CRM of Ho₂O₃

Certified value	<i>U</i> certificate	Measured value	<i>U</i> measured	Normalized error
241.12	0.05	241.18	0.09	0.60
249.89	0.05	249.93	0.09	0.40
278.13	0.05	278.17	0.09	0.40
287.22	0.05	287.26	0.09	0.40
333.48	0.05	333.50	0.11	0.17
345.38	0.05	345.43	0.10	0.45
361.25	0.05	361.30	0.09	0.50
385.61	0.04	385.67	0.08	0.66
416.25	0.05	416.32	0.08	0.75
451.45	0.05	451.38	0.10	0.64
467.82	0.04	467.84	0.07	0.26
485.23	0.04	485.30	0.07	0.92
536.56	0.04	536.63	0.07	0.84
640.50	0.04	640.55	0.07	0.59

3.1. Characterization

The uncertainty calculation of Ho₂O₃ CRM candidate will be evaluated by each laboratory using its own standards. The following uncertainty sources will be considered: (a) measurements repeatability, (b) SRM-2034 traceability, (c) spectrophotometer calibration uncertainty.

The characterization uncertainty (u_{char}) will be calculated as the square root of the sum of squares of each laboratory uncertainty, according to (1).

$$u_{char} = \sqrt{u_{LAB1}^2 + u_{LAB2}^2} \quad (1)$$

3.2. Non-homogeneity

In order to estimate the degree of non-homogeneity of the produced batch, the data obtained was analyzed using the single-factor analysis of variance (ANOVA), which allows the calculation of the standard deviation between the

units of CRM and the standard deviation of the repeatability of the measurement method.

Measurement uncertainty of non-homogeneity (u_h) is a function of the mean square (M) values between the ampoules (M_b) and within the ampoules (M_w). If M_b is greater than the M_w , the uncertainty is calculated by (2). If M_w is greater than M_b , the uncertainty can be obtained by (3).

$$u_h = \sqrt{\frac{M_b - M_w}{n}} \quad (2)$$

$$u_h = \sqrt{\frac{M_w}{n}} \cdot \sqrt{\frac{2}{df_{M_w}}} \quad (3)$$

where n is the number of repeated measurement on the same ampoule and df_{M_w} is the M_w degree of freedom [7].

3.3. Stability

The stability assessment will be analyzed using the linear regression tool to evaluate data and estimate the uncertainty obtained in the stability studies. For stability studies, it will be checked the absence of a significant trend of the CRM value over the time.

Measurement uncertainties for the short-term (u_{ss}) and long-term (u_{ls}) stabilities are determined by multiplying the standard error (e_{sd}), obtained from the linear regression calculations, by the studied time (t) (in the case of the short-term study) or by the estimated time for material validity (t) (in the case of the long-term study), as shown in (4) [7].

$$u_{ss} = e_{sd} \cdot t \text{ and } u_{ls} = e_{sd} \cdot t \quad (4)$$

3.4. CRM uncertainty

Uncertainty evaluation of the produced CRM will

be finally obtained as described in (5).

$$U = k \cdot \sqrt{u_{char}^2 + u_h^2 + u_{ss}^2 + u_{ls}^2} \quad (5)$$

where U is the expanded uncertainty of the CRM and k is the coverage factor for an approximately 95% of confidence level [7].

4. CONCLUSION

In this article it was emphasized the importance of traceability and uncertainty evaluation in the Ho_2O_3 CRM development, since it is used in spectrophotometric wavelength measurements for assuring accuracy and reliability on chemical and photometric measurements. It was presented all the necessary steps for the metrological certification of this material that is being produced as a future CRM by the first time in Brazil. Preliminary results from the first produced batch showed good agreement with the NIST SRM-2034 reference material and the ensuing characterization is under way.

REFERENCES

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