

Studies to develop certified reference material to calibrate spectrophotometer in ultraviolet region

Felipe Carvalho da Conceição¹, Paulo Paschoal Borges¹ and Juliana Freitas Santos Gomes²

¹ National Institute of Metrology, Quality and Technology- Inmetro/Chemical Metrology Division/Electrochemistry Laboratory;

² National Institute of Metrology, Quality and Technology- Inmetro/Optical Metrology Division/Radiometry and Photometry Laboratory.

E-mail: fcconceicao@inmetro.gov.br

Abstract: Spectrophotometry is an used technique in multiples laboratories around the world. Quantitative determination of a high number of inorganic, organic and biological species can be made with this technique using calibrated spectrophotometers. International standards require the use of optical filters to perform the calibration of spectrophotometers. One of the recommended materials is the crystalline potassium dichromate (K₂Cr₂O₇) for calibration or verification of spectrophotometers in the ultraviolet (UV) spectral regions. This paper presents the results concerning the feasibility in producing a certified reference material (CRM) of crystalline potassium dichromate to be used as calibrator of spectrophotometers before using in quantitative analyses.

Keywords: Spectrophotometer, certified reference material, potassium dichromate, ultraviolet regions, calibration.

1. INTRODUCTION

The absorption molecular spectrometry (also called spectrophotometry) in the ultraviolet (UV) spectral regions is very used for quantitative determining of a high number of inorganic, organic and biological species in chemical laboratories, petrochemical, environmental, forensic and clinic around the world. It is based on the transmittance or absorbance measurements carried out in spectrophotometer, which is an instrument that relates the concentration of determined substance with the quantity of the

absorbed or transmitted radiation in specific wavelength, that traversed transparent container with length of path defined [1] according to the Lambert-Beer's law as below:

$$A_a = a_a \times b \times c \quad (1)$$

Where, A_a is the apparent absorbance; a_a , apparent absorptivity; b , length of path and c , the concentration. The term named apparent was introduced together with the parameters absorbance and absorptivity because the effect related to the buoyancy correction for mass and also internal reflections of light in the quartz cuvette were not considered in the measurements.

For guaranteeing of reliability and metrological traceability from measurement results, the ABNT NBR ISO/IEC 17025 standard states that all equipment, which has an important effect in the accuracy and reliability of the measurement results of testing, calibration or sampling, shall be calibrated before being used [2].

One of the statements concerning the spectrophotometers in the regional standard ASTM E925[3] says that it is of own analyst's responsibility verify and validate either if the instrument is running correctly or if it is capable to provide acceptable analytical results. The verification of the performance of the instrument shall be done with the use of certified reference materials (CRMs). These CRMs must have optical properties very well characterized to be used for that purpose.

Currently, the National Institute of Standards & Technology (NIST) provides the SRM 935a [4]. This standard reference material is the crystalline potassium dichromate, from which solutions with specific concentrations to the wavelengths in the spectral regions of UV are prepared. These standard solutions are used to evaluate the performance of the spectrophotometers in the UV regions.

Due to the importance of verifying the performance of the spectrophotometers to regular time interval, as well as to the National Institute of Metrology, Quality and Technology (Inmetro) was granted the calibration and measurement capability (CMC) for high purity potassium dichromate, CRM 8477, the Electrochemistry Laboratory from the Chemistry Metrology Division (Dquim) together with the Radiometry and Photometry Laboratory from the Optical Division (Diopt) are developing the CRM of crystalline potassium dichromate.

The main goal of this work is to present the fundamental studies needed to develop the CRM of crystalline potassium dichromate in Brazil,

since this CRM will contribute to guarantee the accuracy and linearity of the absorbance scale to the spectrophotometers, through which analytical measurement results will be provided with metrological traceability and reliability.

2. BATCH OF THE CANDIDATE OF CRM OF POTASSIUM DICHROMATE

2.1. Feasibility studies

Initially, solutions of potassium dichromate ($K_2Cr_2O_7$) in $0.001 \text{ mol}\cdot\text{L}^{-1}$ perchloric acid ($HClO_4$) medium were prepared. The concentrations of the $K_2Cr_2O_7$ were 20, 40, 60, 80 and $100 \text{ mg}\cdot\text{kg}^{-1}$. These concentrations will provide absorption in the specific wavelength range needed to verify the performance of the spectrophotometers in the UV regions. With the measurement results of absorbance for each solution, there was calculated the apparent absorptivity as describes in (1) and the results were compared to the values shown in the NIST certificate SRM 935a.

2.2. Stability of the solutions

It was prepared, in addition, 1 L of two new solutions of $K_2Cr_2O_7$ in $0.001\text{mol}\cdot\text{L}^{-1}$ $HClO_4$ either in the lowest level of concentrations, $20 \text{ mg}\cdot\text{kg}^{-1}$, or in the highest level, $100 \text{ mg}\cdot\text{kg}^{-1}$, for the stability study. This study is needed to verify the bias in the parameter of apparent absorptivity along the time. This study is very important for the consumer to know if the dichromate solutions will remain their optical properties constant a long the time.

2.3. Batch preparation

A batch contained 64 bottles of the candidate of CRM was prepared. Firstly, 1 kg of the salt of $K_2Cr_2O_7$ was mixed and manually homogenized; after, 15 g of the material was weighed in an analytical balance and was filled in each glass bottle, which was numbered in the order of filling. Finally, 4 bottles were at random selected

from the batch for the studies of homogeneity, characterization and stability of the solutions.

2.4 Homogeneity and characterization

Both homogeneity and characterization studies are being performed. The uncertainty related to the both studies will be added to the uncertainty of the CRM. The apparent absorptivity of the solutions in five different concentrations of $K_2Cr_2O_7$ was chosen as the property value. The inhomogeneity of the batch will be inferred by using the statistical test of One-way ANOVA. The characterization of the candidate CRM will be carried out by an comparison test performed by two laboratories.

3. EXPERIMENTAL

3.1. Reagents

High purity $K_2Cr_2O_7$ (99.5%) from Sigma-Aldrich and $HClO_4$ P.A. (70-72%) from Merck were used. All solutions were prepared using deionized water from Elga® model Option-Q with electrolytic conductivity lower or equal to $1.0 \mu S cm^{-1}$.

3.2. Equipment

The apparent absorbances were measured by UV/VIS Spectrophotometer Lambda 25 from Perkin Elmer®, using quartz cell from Perkin Elmer® with length of path of 1.0 cm. The potassium dichromate solutions were prepared weighing the material using analytical balance both from Mettler Toledo® with resolution 0.001 g (PR-1203) or a microbalance with resolution of $0,1 \mu g$ (UMX-5) when necessary.

3.3. Methodology

The utilized methodology was as follows: Initially, $K_2Cr_2O_7$ solutions were prepared in $0.001 mol \cdot L^{-1} HClO_4$ using the CRM of potassium dichromate from Inmetro (MRC 8477) in the following concentrations: $20 mg \cdot kg^{-1}$, $40 mg \cdot kg^{-1}$, $60 mg \cdot kg^{-1}$, $80 mg \cdot kg^{-1}$, and $100 mg \cdot kg^{-1}$. After then, measurements of apparent

absorbance in triplicate were done in the specific wavelengths in the UV regions: 235 nm ($1 nm = 10^{-9} m$), 257 nm, 313 nm, 345 nm and 350 nm. Finally, from the apparent absorbance values, the apparent absorptivities were calculated by using Eq. (1) for each wavelength measured.

4. RESULTS AND DISCUSSION

Figure 1 shows the absorption spectrum for specific concentrations of the solutions (range $20-100 mol \cdot kg^{-1}$). It can be seen that the apparent absorbance increases in each wavelength measured as soon as the concentration is raised. Using these values of apparent absorbance measured, it was calculated the correspondent apparent absorptivity values by equation (1). The values of apparent absorptivity reached in this work were compared to the values of absorptivity presented in the certificate of the SRM 935a from NIST as shown in the table 1.

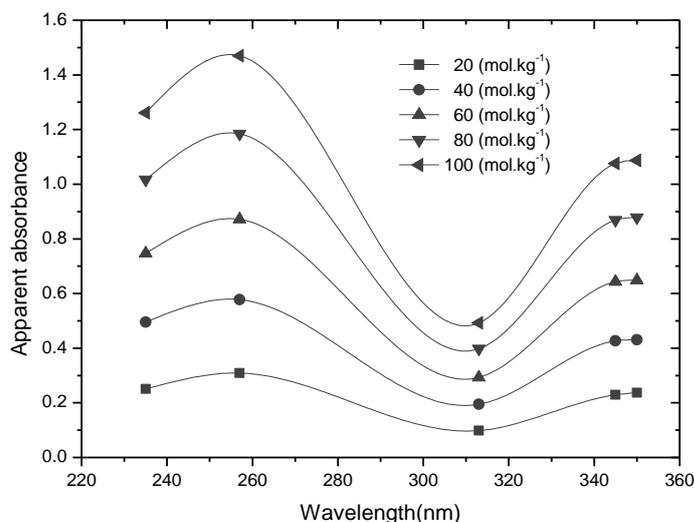


Figure 1. Absorption spectra of potassium dichromate solutions in perchloric acid medium.

Although the spectral bandwidth (SBW) used in this work was constant and equal to 1 nm, the results were comparable do the results showed in the NIST's certificate. In the certificate SRM 935a the SBWs varied in the range of 0.8 to 1.2 nm. On the other hand, the ASTM E-925

standard recommends that the SBW should not be higher than 2 nm, therefore the comparability of the measurement results can be acceptable. From table 1, it can be seen that the relative error was lower than 1%, which shows that it is viable to develop this new CRM of crystalline potassium dichromate in Brazil.

Table 1. Apparent absorptivity and the relative error considering this work and the SRM 935a.

Concentration (mg·kg ⁻¹)	λ (nm)	a_a (kg·cm ⁻¹ ·g ⁻¹)	Error ¹ (%)
20	235	11.879	0.25
	257	14.659	-0.88
	313	4.644	0.32
	345	10.868	-0.37
	350	11.231	-0.51
40	235	12.329	-0.20
	257	14.387	-0.48
	313	4.848	-0.76
	345	10.643	-0.38
	350	10.726	-0.41
60	235	12.306	0.33
	257	14.366	0.05
	313	4.823	-0.16
	345	10.592	0.09
	350	10.696	-0.04
80	235	12.418	-0.22
	257	14.461	-0.22
	313	4.857	-0.75
	345	10.610	-0.08
	350	10.720	-0.18
100	235	12.462	-0.23
	257	14.527	-0.29
	313	4.861	-0.62
	345	10.628	-0.26
	350	10.743	-0.30

¹ Absorptivity of this work divided by the absorptivity from NIST.

For 5 months, the stability of the K₂Cr₂O₇ solutions in 0.001 mol·L⁻¹ HClO₄ medium in the concentrations of 20 mg·kg⁻¹ and 100 mg·kg⁻¹ is showed in figure 2.

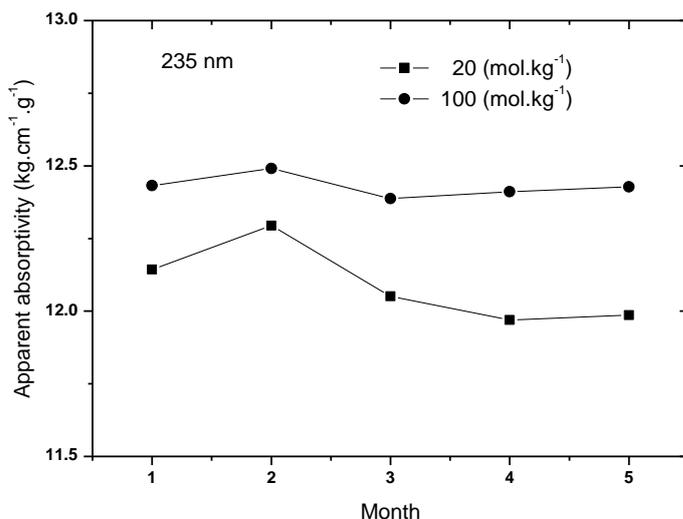


Figure 2. Stability of the dichromate solutions due to the apparent absorbance parameter.

The wavelength of 235 nm was considered as an example. All the data of apparent absorptivity was considered normally distributed by Shapiro-Wilk test. By regression analysis, the values of apparent absorptivity measured in the solutions were considered stable (p -value > 0.05) for a confidence level of 95%. Because of that, the K₂Cr₂O₇ solutions can be considered stable for 5 months. Considering the results of feasibility studies, a batch of a candidate CRM of crystalline potassium dichromate was prepared. Samples from this batch are being used in the certification studies. The process of certification will be subject to a next work.

5. CONCLUSION

Spectrophotometry is an analytical technique very well used in diverse laboratories in the country. With the development of the CRM of crystalline potassium dichromate, the laboratories can guarantee better accuracy in the spectrophotometric analyses in diverse areas, for example, the petrochemical laboratories for analyzing some quality parameters of biofuels needed to be in accordance with the specifications of National Agency of Oil, Natural Gas and Biofuels (ANP).

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6. REFERENCES

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