

Characterization of potassium dichromate solutions for spectrophotometer calibration

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Abstract: Spectrophotometric analysis in the ultraviolet (UV) region is used in the determination of several quantitative and qualitative parameters. For ensuring reliability of the analyses performed on the spectrophotometers, verification / calibration of the equipment must be performed periodically using certified reference materials (CRMs). This work presents the characterization stage needed for producing this CRM. The property value characterized was the absorbance for the wavelengths in the UV spectral regions. 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.

Keywords: Characterization; CRM; potassium dichromate; calibration; spectrophotometer.

1. INTRODUCTION

It is usually recommended testing the spectrophotometer's performance using certified reference materials (CRMs) and it is also important that the technical analyst finds ways to validate if the instrument is operating properly or if it is capable to provide acceptable analytical results [1].

Due to the importance of verifying the spectrophotometer's performance in a regular interval of time, the Electrochemical Laboratory from Chemical and Thermal Metrology Division (Dimqt), together working with the Laboratory of Radiometry and Photometry from Optical Metrology Division (Diopt) developed the CRM of crystalline potassium dichromate ($K_2Cr_2O_7$). From this CRM, some acid solutions with

specific concentrations for the wavelengths in the UV spectral regions are prepared. Then, these standard solutions will be used to evaluate the performance of spectrophotometers in the UV regions [2].

Acid solutions from this CRM must have their optical properties properly characterized to be used for this purpose. The characterization stage is very important to the CRM development [3]. In this stage, the value of the property to be certified is obtained and its measurement uncertainty is evaluated. The uncertainty of the characterization (u_{char}) will contribute to the uncertainty of the CRM.

The characterization stage involves the preparation of five different concentrations of dichromate acid solutions from the batch of the

candidate CRM of $K_2Cr_2O_7$ for measuring the solutions in different equipment, in this case, in two laboratories with different methodologies [3] and by qualified technicians. At the end, the results obtained are compared and an average value from the two laboratories is chosen in order to assure the metrological reliability of the results from the use of $K_2Cr_2O_7$ as a reference material for the verification of the photometric scale of the spectrophotometer in the UV spectral region.

1.2. Objective

This work aims to present the methodology for the characterization of the candidate CRM of $K_2Cr_2O_7$, in order to fulfil one of the production steps for this material to be recognized as a CRM.

2. EXPERIMENTAL

2.1. Batch of candidate CRM of $K_2Cr_2O_7$

Reference material (RM) developed in a batch contained 64 bottles of the candidate CRM of $K_2Cr_2O_7$ was prepared (Figure 1). Firstly, 1 kg of the salt of $K_2Cr_2O_7$ was mixed and manually homogenized; after, 15 g of the material were weighed in an analytical balance and were filled in each glass bottle, numbered in the order of filling. Finally, 4 bottles were at random selected from the batch for the homogeneity, characterization and stability studies. Before preparing the acid solutions, the purity of the $K_2Cr_2O_7$ was determined by coulometric titration (99.921 %) and this value was taken into account for calculating the concentration of the solutions.



Figure 1. Batch of the candidate CRM of $K_2Cr_2O_7$ [4].

2.2. Potassium dichromate acid solutions

Potassium dichromate solutions from the batch of the candidate CRM of $K_2Cr_2O_7$ in 0.001 mol L^{-1} perchloric acid ($HClO_4$) medium were prepared gravimetrically. The concentrations of the $K_2Cr_2O_7$ were 20 mg kg^{-1} , 40 mg kg^{-1} , 60 mg kg^{-1} , 80 mg kg^{-1} and 100 mg 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, it can be calculated the apparent absorptivity according to the Lambert-Beer's law (equation 1), where the concentrations are correlated with the absorbance.

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

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.

Thus, acid solutions prepared from different samples of the candidate CRM of $K_2Cr_2O_7$ were measured in two spectrophotometers at Inmetro in different laboratories and the results were compared each other.

For guaranteeing the reliability and metrological traceability from measurement results, all instruments, which had an important effect in the accuracy and reliability of the measurement results of testing, were calibrated before being used.

3. RESULTS

3.1. Characterization

Acid solutions from sample 23 and 57 from the

batch of the candidate CRM of $K_2Cr_2O_7$ prepared at different concentrations were measured in two different spectrophotometers, with different technicians.

The values obtained in the absorbance measurements are showed in table 1. The final result is the average absorbance (A) measured for each concentration, as well as the expanded uncertainties U (A) associated with each measurement, according to the GUM [5].

Table 1. Samples 23 and 57: comparing results.

	λ (nm)	Sample 23		Sample 57		Error ^a	En ^b
		A	U	A	U		
20 mg kg ⁻¹	235	0.252	0.003	0.262	0.018	0.010	0.56
	257	0.290	0.003	0.303	0.018	0.014	0.75
	313	0.100	0.003	0.105	0.016	0.004	0.28
	345	0.215	0.004	0.225	0.018	0.010	0.55
	350	0.217	0.004	0.227	0.018	0.010	0.57
40 mg kg ⁻¹	235	0.511	0.006	0.519	0.010	0.008	0.73
	257	0.593	0.007	0.601	0.012	0.007	0.53
	313	0.200	0.004	0.203	0.008	0.003	0.29
	345	0.440	0.005	0.440	0.010	0.000	0.03
	350	0.444	0.005	0.443	0.010	0.000	0.03
60 mg kg ⁻¹	235	0.743	0.009	0.748	0.014	0.006	0.34
	257	0.865	0.012	0.871	0.014	0.006	0.30
	313	0.290	0.003	0.293	0.009	0.002	0.25
	345	0.640	0.007	0.641	0.012	0.002	0.12
	350	0.645	0.008	0.648	0.012	0.002	0.16
80 mg kg ⁻¹	235	0.999	0.017	1.011	0.016	0.011	0.49
	257	1.164	0.025	1.176	0.021	0.012	0.38
	313	0.390	0.004	0.394	0.010	0.004	0.37
	345	0.856	0.012	0.862	0.014	0.006	0.32
	350	0.865	0.012	0.872	0.014	0.007	0.36
100 mg kg ⁻¹	235	1.270	0.032	1.255	0.016	0.015	0.43
	257	1.480	0.051	1.460	0.021	0.021	0.38
	313	0.493	0.005	0.489	0.010	0.005	0.42
	345	1.085	0.021	1.067	0.014	0.018	0.73
	350	1.097	0.021	1.079	0.014	0.018	0.69

^a Error = $A_{\text{sample 57}} - A_{\text{sample 23}}$; ^b En, normalized error.

The results in table 1 are in accordance with

the ASTM E925 [1]. At the table 1 can also be seen the error and the normalized error obtained.

The environmental conditions during the measurements were $T = (25.1 \pm 0.8) ^\circ\text{C}$ and $RH = (58.2 \pm 2.6) \%$. Each laboratory calculated its own uncertainty.

3.1.2 Apparent absorptivity uncertainty

If it were necessary to use the results in apparent absorptivity, the laboratories need to determine the apparent absorptivity uncertainty that will be composed by absorbance (A), optical path (b) [cm] and concentration (c) [g kg^{-1}] derived from equation (1).

The influence due to the optical path can be calculated from measurements in a set of n cuvettes chosen at random from those used in the analyses. Each set cuvette can be measured n times and the mean of n measurements to be use for calculating the optical path value.

In this case, as the solution was prepared gravimetrically, so the influence due to the concentration considers only the uncertainties of the balance and the purity. The value to be considered as influence due to the concentration will be 0.0001 g kg^{-1} . Table 2 shows the apparent absorptivity uncertainty budget to 20 mg kg^{-1} of $K_2Cr_2O_7$ solution as an example.

Table 2. Apparent absorptivity uncertainty budget to the 20 mg kg^{-1} solution.

Variable	Unit	Value	Uncertainty Contribution [$\text{kg}\cdot\text{cm}^{-1}\cdot\text{g}^{-1}$]
Absorbance	1	0.0028	2.76×10^{-5}
Light path	cm	0.0021	-1.00×10^{-2}
Concentration	[g kg^{-1}]	0.0001	-5.01×10^{-4}
$u_c(a_a)$	0.010026 $\text{kg m}^{-1} \text{g}^{-1}$		
k	2.09		
U (20 mg kg^{-1})	0.021 $\text{kg m}^{-1} \text{g}^{-1}$		

4. CONCLUSION

In the characterization stage of the candidate CRM of $K_2Cr_2O_7$, measurements of the solutions were carried out at concentrations of 20 mg kg^{-1} ,

40 mg kg⁻¹, 60 mg kg⁻¹, 80 mg kg⁻¹ and 100 mg kg⁻¹ in two spectrophotometers in different laboratories. The results were compared in order to ensure reliability of the studied material. The analysis of the results shows that the measurements are compatible, taking into account the different measurement methodologies used in each instrument, and also by different technicians.

The normalized errors (E_n) found were less than 1.0 ($E_n < 1.0$), which attesting the metrological reliability of the results obtained from using of crystalline potassium dichromate as a reference material for photometric scale of spectrophotometers in the UV region.

The characterizations of potassium dichromate solutions considering absorbance as property value will be declared in the certificate.

This stage proves the technical feasibility of Inmetro to produce and to supply to the national and international market a CRM of potassium dichromate for verifying the linearity of commercial spectrophotometers in the ultraviolet region, thus guaranteeing the traceability and reliability of the results of the measurements made by laboratories using the spectrophotometric technique in the country.

On the basis of the results obtained, Inmetro is able to produce the CRM of potassium dichromate, similar in quality to that of

international producers, sparing the plaintiffs from the bureaucratic drawbacks of imports. In addition, being the only one available in the domestic market, it is reasonable to expect that the demand for the product will gradually increase.

5. REFERENCES

- [1] ASTM E925 – 09(2014), Standard Practice for Monitoring the Calibration of Ultraviolet Visible Spectrophotometers whose Spectral Bandwidth does not Exceed 2 nm.
- [2] NBS Special Publication 260-54 – SRM Certification and use of acidic potassium dichromate solutions as an ultraviolet absorbance standard - SRM 935, 1977.
- [3] ISO 17034: 2016 General requirements for the competence of reference material producers.
- [4] CONCEIÇÃO, F. C., “Estudos com soluções de dicromato de potássio visando desenvolver material de referência certificado para calibração de espectrofotômetros na região do ultravioleta” - Monografia de conclusão do Curso Técnico em Metrologia do Inmetro, SEEDUC-RJ, CECO, 2015.
- [5] GUM: 2008, Guia para a expressão de incerteza de medição. Avaliação de dados de medição. Rio de Janeiro, Inmetro, 2012.
- [6] <http://kcdb.bipm.org/appendixC/>