Preparation and Validation of Potassium Dichromate in Dilute Sulfuric Acid as a Secondary Standard for UV-Visible Spectrophotometer Calibration

Pranee Nandhasri* and Tanet Pakeetoot
Department of Medical Science, Faculty of Science, Rangsit University.
* Corresponding author.

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ABSTRACT Potassium dichromate in dilute sulfuric acid is a common reference standard for the calibration of uv-visible spectrophotometer. However the reproducibility and accuracy of the solution is difficult to achieve for laboratories that do not have experienced personnel. A solution of potassium dichromate in 0.01 N sulfuric acid was prepared and validated for distribution as a secondary reference material.

KEYWORDS: spectrophotometer, potassium dichromate, calibration, validation.

INTRODUCTION

Potassium dichromate, an orange color chemical, at the specific concentration of 60 mg/ l in 0.01 N sulfuric acid is used as the standard for the calibration of uv-spectrophotometer. The absorbance of this standard should be 0.747, 0.869, 0.293 and 0.644 at the wavelength of 235, 257, 313, and 350 nm respectively.[1] The maximum deviation value should not be more than ± 1 % of the full scale absorbance unit at every range of triplicate measurement.

In order to obtain potassium dichromate solution (PDCS) as the working standard conforming to the standard value as mentioned above, it is necessary to have precise and accurate equipment and also well trained personnel with good laboratory practice (GLP) and good measurement practice (GMP). The reference standard material (RSM) for uv-spectrophotometer from the recognized supplier costs about 165,000 Bath per laboratory per year.

The objective of this project is to produce the PDCS as working standard for uv-spectrometer calibration which could result in a saving of 50 million Baht per year for about 300 laboratories in the country.

MATERIALS AND METHODS

1. Materials

1.1 Sulfuric acid, analytical grade,0.01 N

1.2 Potassium dichromate, 99.99 % analytical grade, Merck ,60 mg/l in concentration is prepared by dissolve exactly 60 ± 0.25 mg, weighing out by the calibrated analytical balance, of potassium dichromate (dried) in 1 liter of 0.01 N sulfuric acid (1.1). Store this potassium dichromate solution (PDCS) in a brown bottle at 25°C. This PDCS was used in all validations (3.2).

1.3 A set of Hellma: Secondary Spectrophotometric Calibration Standard Grey glass filter F2, F3, F4 (SSCS: F2,F3,F4) for visible range absorbance calibration and Holmium oxide (F1) for uv-visible-spectrum calibration which are traceable to a set of NIST 930B standard.[2]

2. Equipments

2.1 Reference standard equipment (RSE), Shimadzu; UV-2501PC Spectrophotometer.

2.2 Working standard equipment (WSE) , Milton Roy: Spectronic 1001 Plus.

3. Methods

There are two parts in the project :firstly ; calibration methods, the calibration of the instrument, using the Hellma secondary standard traceable to NIST standard, and secondly ; the validation method of the working standard , potassium dichromate solution standard (PDCS).

3.1 The calibration method to calibrate the reference standard equipment (RSE)

3.1.1 The calibration of the RSE was performed by using a set of Hellma Certified Secondary Standard (SSCS: F2, F3, F4) which was traceable to NIST primary standard.[2] The absorbance of F2, F3 and F4 at wavelengths 440,465,546,590 and 635 nm are taken and compared to the Hellma certified value.

The SSCS: F1, holmium oxide standard was used

to scan the spectrum accuracy of equipment RSE between 250 to 650 nm.

3.1.2 The calibration program for checking of the instrument accuracy is established by calibrating with secondary standard (SSCS: F2, F3, F4) and SSCS: F1 every time when performing the calibration of the PDCS , and at least twice a month.

3.2 The validation of the working standard PDCS:

3.2.1 Validation of temperature dependent factor at 40, 50, and 60°C ;

3.2.2 Validation of time dependent factor at 5, 10, 15, 20 and 25 hours. The absorbance (A) or optical density (OD) were measured 14 times (N = 14) in all the methods 3.2.1, and 3.2.2 at the wavelength of 235, 257, 313 and 350 nm

3.2.3 Validation of PDCS stability from one which was treated at 50°C for 20 hours. The absorbance measurement of PDCS at the wavelength of 235, 257, 313 and 350 nm were run 14 times (N = 14) during six months period.

Results and Discussion

Hellma secondary standard F2, F3 and F4 used for calibrating of the reference standard equipment (RSE) at the wave length of 440, 465, 546, 590 and 635 nm during one year are shown in the Fig 1. The average absorbance result of sixteen (N = 16) measurements, F2-, F3-, F4-RSE, from the reference standard equipment (RSE) are conformed to the Hellma certified standard volume (F2-, F3-, F4-SSCS)

The uv-visible-spectrum of holmium oxide

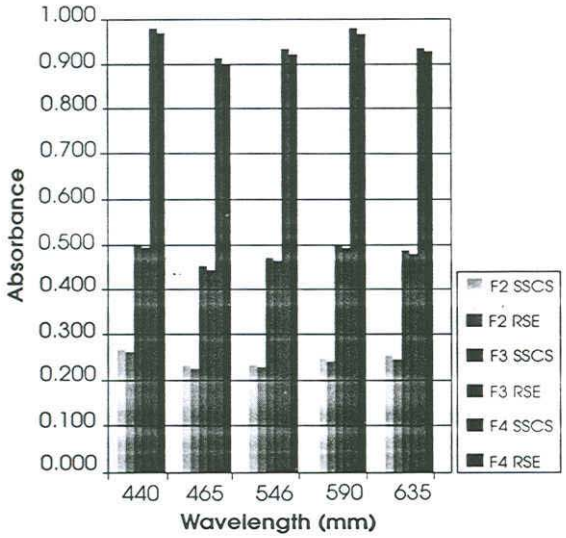

Fig 1. The absorbance value comparison between Hellma's certified value (F2,F3,F4-SSCS) and the calibrated value (F2, F3, F4- RSE) which measured by the reference standard equipment (RSE), UV2501PC.

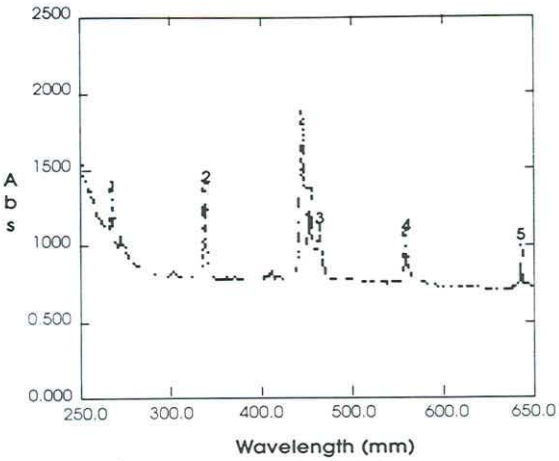

Fig 2. Wavelength scanning of holmium oxide (F1) Hellma secondary spectronic calibration standard.

Measuring Mode	:	Abs.
Scan Speed	:	Slow
Slit Width	:	1.0
Sampling Interval	:	0.1

No.	Wavelength (nm.)	Abs.
1	279.00	1.021
2	361.00	1.072
3	453.00	1.018
4	536.00	0.699
5	638.00	0.562

standard (F1) at the wavelength between 250-650 nm, during one year period, all measurement results by SIR (Shimadzu -UV-2501 PC) are comformed to the certified wavelengths of Hellma.[2] (Fig 2)

The average absorbance values of PDCS working standard measured by Shimadzu UV-2501 PC (RSE) and Spectronic 1001(WSE) at wavelengths 235, 257, 313 and 350 nm, were in the range of the control RSV,[1] (Table 1).

The absorbance of PDCS at 5,10,15,20 and 25 hours have significant level ($P<0.05$) correlation at all temperature of 40, 50 and 60°c at 95%. This significant correlation showed no different changes in absorbance due to the variation of time and temperature. Fig 3 show the best conditions of PDCS secondary standard at the activating temperature 40 – 50°C for 20 hours. Perhaps there is an equilibrium between $Cr_2O_7^{-2}$ and $HCrO_4^{-1}$ species in solution, and the amount of the two species in solution depends on the concentration of the total dichromate in the solution.

Fig 4 Stability of Potassium dichromate solution (PDCS) during six months period, the absorbance measured at wavelengths 235, 257, 313 and 350 nm.

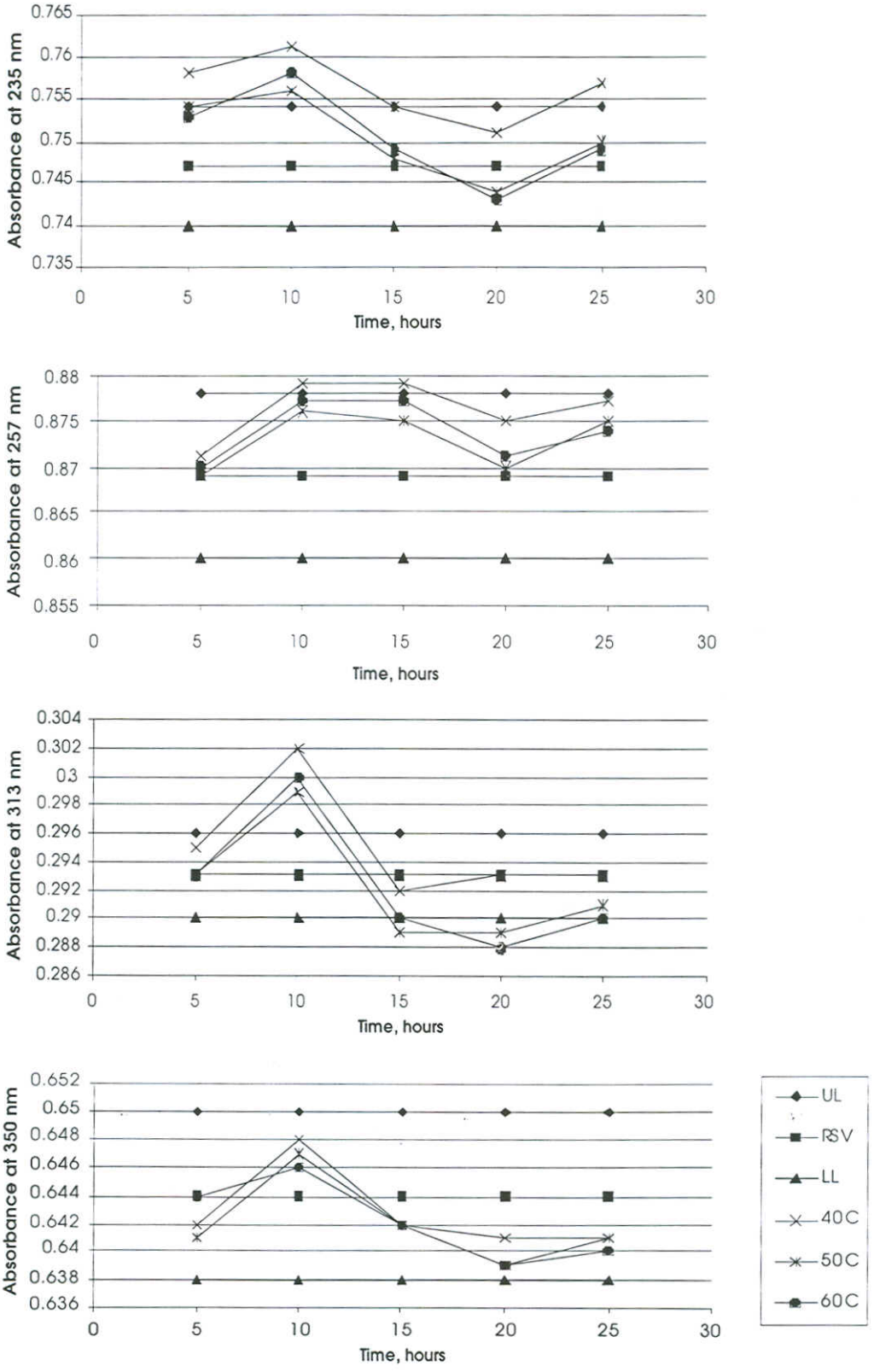

Fig 3. Comparison of mean absorbance (n=14) at wavelengths 235, 257,313 and 350 of potassium dichromate solution (PDCS) treated at 40, 50 and 60°C for 5, 10, 15, 20 and 25 hours to the reference standard values(RSV) and their upper level(UL), lower level (LL).

Table 1. Absorbance value (N=14) of PDCS standard measured by Shimadzu UV-Spectrophotometer UV-2501 PC and Milton Roy Spectrophotometer (Spectronic 1001) compared to the Reference Standard Value.

Wavelength(nm)	Absorbance			
	235	257	313	350
UV-2501 PC	0.752±0.007	0.874±0.006	0.293±0.003	0.642±0.003
Spectronic 1001	0.756±0.010	0.884±0.010	0.308±0.015	0.652±0.006
Reference Standard Value*	0.747±0.007	0.869±0.009	0.293±0.003	0.644±0.006

* Garfield FM (1991).

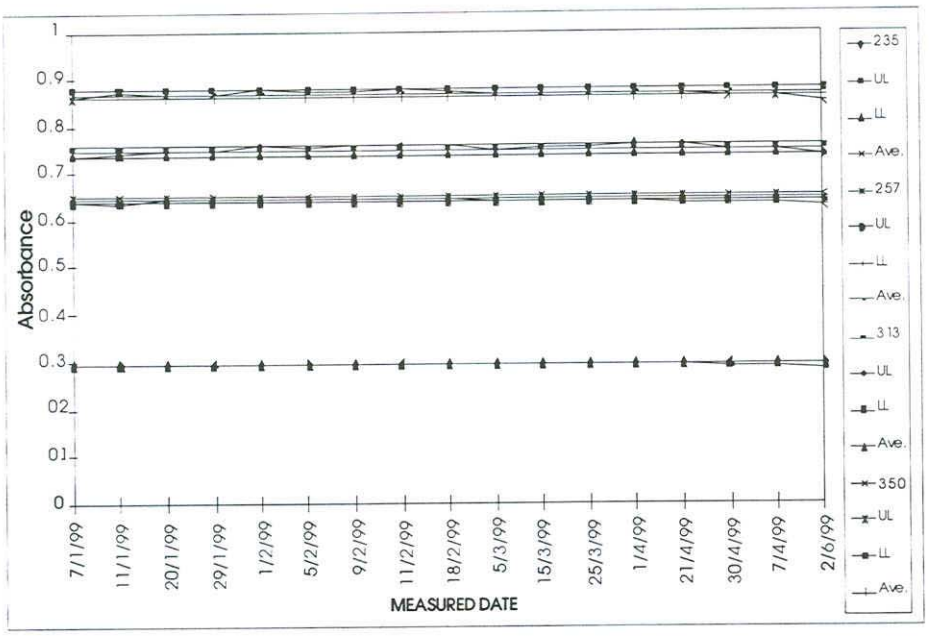

Fig 4. Stability of Potassium dichromate solution (PDCS) during six months period, the absorbance measured at wavelengths 235, 257, 313 and 350 nm.

The PDCS activated at 50°C for 20 hours is used for stability validation and for the proficiency test on the calibration of uv-spectrophotometer. The PDCS stability of six months period is shown in Fig 4. The calibration of the standard instrument SIR(Shimadzu: UV-2501 PC) at wavelengths 235, 257, 313 and 350 nm by the other set of Hellma's reference materials and the uncertainties of PDCS are reported in the 9th International Metrology Congress 1999 [3]. The proficiency test is reported in the separated paper of this journal[4].

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