

International Comparisons for Coulometric Determinations of Dichromate Used to Develop Certified Reference Material for Oxidation-Reduction Titration

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Inicialmente, para adquirir experiência na determinação coulométrica da pureza do dicromato, realizou-se uma comparação bilateral entre os institutos nacionais de metrologia (INM) do Brasil e da Rússia. Em seguida, objetivando comparar os resultados das medições do dicromato de potássio ($K_2Cr_2O_7$) entre os INM que utilizam a coulometria com elevada precisão para certificar materiais de referência (MR) de compostos puros, o Inmetro participou de uma comparação-chave denominada CCQM-K96. A partir dessas comparações, certificou-se um lote do MR de $K_2Cr_2O_7$. Este trabalho objetiva apresentar os resultados das comparações internacionais, bem como os estudos necessários ao desenvolvimento do material de referência certificado (MRC) de $K_2Cr_2O_7$, tornando-o um padrão primário para titulações de oxirredução. Para o lote certificado, considerou-se tanto os estudos de homogeneidade quanto de caracterização, obtendo-se o valor da pureza, em fração mássica do $K_2Cr_2O_7$ de $99,974\% \pm 0,011\%$, para $k = 2$ e probabilidade de abrangência de aproximadamente 95%.

Initially, for acquiring experience in determining the purity of the dichromate by coulometry, a bilateral comparison between the national metrology institutes (NMIs) from Brazil and Russia was carried out. Next, to evaluate the comparability of the measurement results among the NMIs that use high-precision constant-current coulometry for certifying reference materials (RMs) of pure compounds, National Institute of Metrology, Quality and Technology (Inmetro) participated in a key-comparison named CCQM-K96. Because of both comparisons, a batch of the RM of $K_2Cr_2O_7$ was certified. This work aims to present the international comparison results, as well as the studies needed to develop a certified reference material (CRM) of $K_2Cr_2O_7$ for redox titrations. In the certification of the batch, studies of homogeneity and characterization were considered. The $K_2Cr_2O_7$ batch was certified in mass fraction of $99.974\% \pm 0.011\%$, for $k = 2$ and coverage probability of approximately 95%.

Keywords: certified reference material, precise coulometric titration, potassium dichromate, comparability

Introduction

The Chemical Metrology Division of the National Institute of Metrology, Quality and Technology (Inmetro) must, among other main duties, develop, produce, and provide certified reference materials (CRMs) for the community to ensure the quality of chemical analyses. The Electrochemistry Laboratory¹ is located within the facilities on campus. Three primary methods of measurements^{2,3} were used including the primary system of coulometry (PSC).⁴ The PSC ensures the traceability of measurement

results by the International System of Units (SI).⁵ This primary system of measurement is considered the standard for amount content determinations because it is utilized at a high-accuracy and high-precision level.⁶⁻⁸ Similar systems are used by the national metrology institutes (NMIs) for certification of pure chemical compounds called primary standards or CRMs. These CRMs are used by the chemical laboratories aiming to obtain reliable measurement results, transfer traceability to the measurements, and validate methods of analysis or calibration.⁹ Some CRMs were developed by Inmetro to guarantee the reliability of the acid-base titrations,¹⁰ such as HCl in content amounts from 1.0 to 0.01 mol kg⁻¹. For new CRMs, their certification

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processes are almost finished, such as with potassium chloride and sodium chloride for precipitation.¹¹ Since accurate certified values and uncertainties are needed to obtain reliable measurements,¹² after the certification process, these CRMs are offered to the scientific, academic, and industrial communities.

In this work, the chemical compound potassium dichromate ($K_2Cr_2O_7$) was selected as a candidate CRM. It is an oxidizing agent used as the primary standard for volumetric analysis of redox reactions.¹³ In addition to the high purity of the primary standards, they are also extremely stable when stored.¹⁴ Therefore, a batch of $K_2Cr_2O_7$ was prepared and the certification process was initiated. This certification process consists of the studies of homogeneity, characterization, and stability.^{9,15} Due to the high stability of the chosen material, stability studies did not need to be carried out.^{9,14} It is important to highlight that, after being certified, the material is constantly monitored to determine whether its property value is stable during its shelf life.^{9,16}

The homogeneity is the condition of uniform structure or composition with respect to one or more specific properties.¹⁶ For studies of homogeneity of the candidate CRM of $K_2Cr_2O_7$, the purity parameter was evaluated and expressed as a mass fraction; this is the weight percentage of potassium dichromate taken from the random samples of the batch material, which is analyzed by coulometric titration.⁶

The characterization is a process of determining the property values of a reference material. For the characterization of a reference material, a primary method of measurement can usually be used with the highest metrological quality, or two independent reference methods. Therefore, the characterization of the candidate CRM of $K_2Cr_2O_7$ was performed only by a high-precision constant-current coulometry, which is considered a primary method.^{6,17-20}

However, a bilateral comparison between the NMIs from Brazil and Russia was carried out in order to acquire experience for coulometric determination of the purity of the dichromate.²¹ Samples from the batch of the candidate CRM of $K_2Cr_2O_7$ were then used in this bilateral comparison.

As an NMI, Inmetro ensures the quality of its results by participating in international comparisons under the Consultative Committee for Amount of Substance-Metrology in Chemistry (CCQM).^{22,23} After the bilateral comparison, the ability of Inmetro to determine the concentration of dichromate using high-precision current-constant coulometry was evaluated in the key comparison CCQM-K96.²⁴ In this key comparison, a sample of potassium dichromate was sent to each of the participating

NMIs by the coordinating laboratory, and the comparability among the NMIs was reported.

This work aims to present the international comparison results, as well as the studies needed to certify a batch of a candidate CRM of $K_2Cr_2O_7$ for redox titrations.

Experimental

The batch of the candidate CRM of $K_2Cr_2O_7$

Potassium dichromate of analytical grade from Spectrum, weighing 500 g, was placed in a plastic tray, mixed, and homogenized with a porcelain spatula. All material was crushed manually by using a porcelain mortar. Once crushed, the material was homogenized, quartered, and, finally, homogenized again. Sub samples of the material totaling approximately 25 g, as weighed in a Mettler Toledo balance with a resolution of 1.0 mg, were filled in glass flasks, sealed with screw caps, and wrapped in a thin layer of Parafilm®. The small batch of the prepared candidate CRM contained 20 identified samples and they were numbered in order of weight.

Homogeneity studies

The homogeneity studies of the candidate CRM of $K_2Cr_2O_7$ were developed expressing the property value as the purity of $K_2Cr_2O_7$ in a mass fraction (%). Its value is related to the concentration expressed in the amount content ($mol\ kg^{-1}$) of $K_2Cr_2O_7$ determined by precise coulometric titration^{6,7} as well as characterization studies.

Three bottles from the batch of the candidate CRM of $K_2Cr_2O_7$ were randomly chosen for the homogeneity studies. Before being used, the samples were dried in an oven at 110 °C for 2 h, and they were then stored inside the desiccator.

For the data treatment, the Grubbs test was first used for the exclusion of outliers that could interfere with the final results. Next, according to the ISO Guide 35 criteria,⁹ the homogeneity of the batch of the candidate CRM of $K_2Cr_2O_7$ was studied using an Analysis of Variance (ANOVA) approach.¹⁶

Characterization studies: precise coulometric titration

The previously described PSC⁸ and precise coulometric titration with biamperometric end-point detection were used as analytical methods for determining the content amount of dichromate in $mol\ kg^{-1}$ or in a mass fraction (%) calculated by using the Faraday constant, $F = 96\ 485.3383\ C\ mol^{-1}$ and $M = 294.1846\ g\ mol^{-1}$, as the molar mass of $K_2Cr_2O_7$. All

reagents were of analytical grade, and deionized water (with electrolytic conductivity equal or less than $0.1 \mu\text{S cm}^{-1}$) was used with all prepared solutions.

The coulometric cell is made of glass with a vertical design containing two separated compartments: the cathodic and the anodic. Figure 1 shows a diagram of the coulometric cell. The anodic compartment (anolyte) was filled with $2.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$. It contained a silica gel (silicate) plug in its base that stayed inside the intermediate compartment (IC), which, in its base, included is a sintered glass plug. The silica gel plug was prepared with silicate solution in $2.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$. Both plugs were needed to separate the catholyte from the anolyte and to maintain the electrolytic contact. The supporting electrolyte (250 mL) was a solution of 0.4 mol L^{-1} ammonium iron (III) sulfate and $2.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$. The indicator electrode used for end-point detection was a double platinum electrode (two Pt wire of 1 mm diameter each). A voltage of 0.050 V was applied between the two wires of the indicator electrode. Two platinum electrodes were immersed in the coulometric cell: a generation electrode (WE) made of a large Pt plate (with dimensions $5 \text{ cm} \times 6 \text{ cm} \times 0.04 \text{ cm}$) and a counter electrode (CE) made of a Pt plate (0.3 mm thickness) with a 1 cm^2 area. The sample of $\text{K}_2\text{Cr}_2\text{O}_7$ was dried at $110 \text{ }^\circ\text{C}$ for 2 h and then cooled in desiccators over silica pellets.

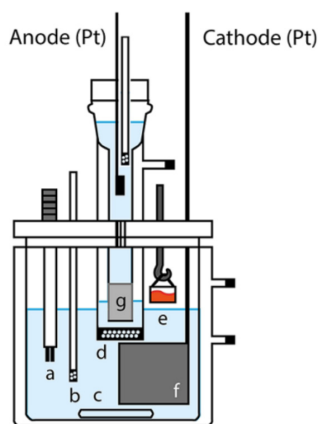


Figure 1. A diagram of the coulometric glass cell used to characterize the candidate CRM of $\text{K}_2\text{Cr}_2\text{O}_7$: (a) a double Pt electrode for indication signal; (b) the argon bubbler; (c) the Teflon stirring bar; (d) the intermediate compartment with a glass frit; (e) a glass basket for inserting the dichromate sample into the cell; (f) the large Pt plate electrode (cathode); (g) a plug of silicate gel where the anolyte with the small Pt plate electrode (anode) and an argon bubbler are localized.

The current required for coulometric titration of a dichromate sample (ca. 0.5 g weighed by using a microbalance Mettler Toledo UMX 5, resolution of $0.1 \mu\text{g}$) was passed on three different phases. For the initial titration, a current of 0.004 A was used, a current of 0.3 A was used for the main titration, and for the final titration, a current of

0.004 A was again used. All the weighing was corrected for buoyancy and the coulometric cell was maintained at $23 \text{ }^\circ\text{C}$ during the experiment. Initially, argon gas with a high purity (99.999%) was passed through the cathodic compartment for deaeration, after it stayed above the compartment during the titration phases.

All the titration phases were carried out with the catholyte stirred by means of a magnetic stirrer. The end-point for each titration was calculated using linear regression up to eight points from the curve $t \text{ (s)}$ versus $I \text{ (mA)}$. Before each measurement, the two electrodes (WE and indicator) were first immersed for 10 min in a concentrated solution of $\text{K}_2\text{Cr}_2\text{O}_7$. After that, they were washed in deionized water and immersed for 10 min in a solution of 0.2 mol L^{-1} ammonium iron (II) sulfate and then they were washed in deionized water. After the first cleaning, the three electrodes (CE included) were immersed in a hot concentrated nitric acid of an analytical grade for 5 min and then washed with deionized water. At the start of each measurement, a volume of approximately $100\text{--}200 \mu\text{L}$ of $0.005 \text{ mol L}^{-1} \text{ K}_2\text{Cr}_2\text{O}_7$ was added to the supporting electrolyte.

Before the main titration began, about 10 min was needed for the $\text{K}_2\text{Cr}_2\text{O}_7$ sample to be dissolved. Fifteen minutes before the main titration was finished, the indicator electrode was rinsed within the cell with deionized water and then taken off the cathodic compartment for cleaning. This precaution was needed to avoid the oxide film formed on the platinum electrode that could affect the behavior of the ferrous-ferric couple,²⁰ therefore causing an error at the end-point detection. Thus, it was immersed for 10 min in a solution of 2.0 mol L^{-1} ammonium iron (II) sulfate and, after, it was washed with deionized water and again taken in the catholyte.

Results and Discussion

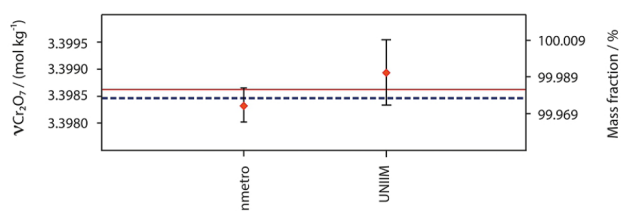
Bilateral comparison

Two samples of potassium dichromate were used for the comparison: the NMI of Brazil (Inmetro) provided one sample and the NMI of Russia (UNIIM) provided another. In this bilateral comparison, both PSCs from each NMI were benchmarked for the further development of CRMs for oxidimetric analysis. Table 1 presents the figure of merits for the samples from Inmetro. In this table, the mean results of the amount content of potassium dichromate (mol kg^{-1}), combined with a standard uncertainty (u_c), a relative combined standard uncertainty ($u_{c,r}$), a relative standard deviation (RSD), and a number of measurements (n) are reported. These results were considered comparable

Table 1. Measurement results of the bilateral comparison of the samples from Inmetro

NMI	Result / (mol kg ⁻¹)	u_c / (mol kg ⁻¹)	$u_{c,r}$ / %	RSD / %	n
Inmetro	3.398329	0.000155	0.005	0.003	7
UNIIM	3.398937	0.000300	0.009	0.009	7

due to the uncertainty of the measurements according to the Guide to the expression of Uncertainty in Measurement (GUM).²⁵ Figure 2 graphically demonstrates the results of the samples from Inmetro achieved by the two NMIs. In this bilateral, the results from Inmetro were used to characterize the K₂Cr₂O₇ from the batch of the candidate CRM, as will be shown going forward.

**Figure 2.** Results of the bilateral comparison of K₂Cr₂O₇ of the samples from Inmetro. The dashed line represents the mean value and the straight line represents the weighted mean value. Error bar corresponds to the expanded uncertainties considering $k = 2$, for a coverage probability of approximately 95%. The mass fractions (%) that correspond to the amount contents can be seen on the right side.

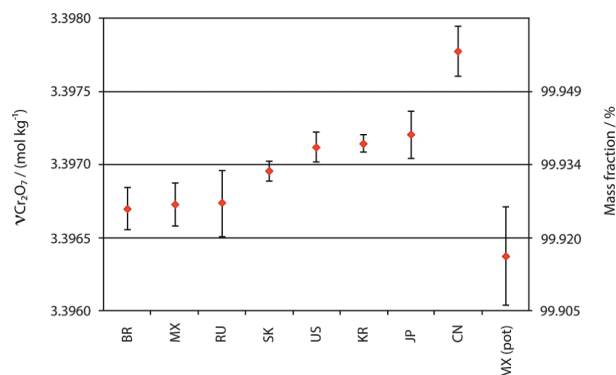
Key comparison CCQM-K96

The complete measurement results of the key comparison CCQM-K96 were reported elsewhere.²⁴ In Figure 3, the results from the participating NMIs are shown. The results of the CCQM-K96 revealed a positive agreement between most participating laboratories for the measurement of potassium dichromate by precise constant-current coulometry. The reference value for this comparison was (3.39705 ± 0.00016) mol kg⁻¹; on the other hand, the value determined by Inmetro was (3.39670 ± 0.00028) mol kg⁻¹, both for $k = 2$, and with a coverage probability of approximately 95%. Therefore, the coulometric titration procedure was evaluated, showing comparability among the NMIs. Because of the positive results achieved by Inmetro in this key comparison, it was possible to certify the batch of the potassium dichromate reliably.

Certification of the candidate CRM of K₂Cr₂O₇

Homogeneity studies

Studies of homogeneity were carried out on three samples randomly chosen from the batch of the candidate CRM and analyzed in four replicates with the use of precise coulometric titration.

**Figure 3.** Results from the participating NMIs in the key comparison CCQM-K96 for determining the amount content of potassium dichromate by precise constant-current coulometry. The x -axis shows the countries from each NMI: Brazil, Mexico, Russia, Slovakia, the United States, Korea, Japan, China, and Mexico (potentiometric titration). All results are illustrated with their combined standard uncertainties.

The results from coulometric titration for the new studies of homogeneity to the candidate CRM of K₂Cr₂O₇ and the ANOVA testing are presented in Tables 2 and 3, respectively.

Table 2. Results from coulometric titration of the candidate CRM for homogeneity testing

n ^a	Mass fraction / %		
	Sample		
	4	9	13
1	99.98048	99.96194	99.97913
2	99.96667	99.98377	99.97281
3	99.98946	99.98240	99.98700
4	99.99352	99.97799	99.98746
Mean	99.98253	99.97652	99.98160
RSD ^b / %	0.012	0.010	0.007

^an: number of replicates; ^bRSD: relative standard deviation.

One can observe that $F < F_{\text{table}}$ for P -value > 0.005 , which is considered to have no significant difference between the samples. Thus, it can be inferred that the samples of the candidate CRM of K₂Cr₂O₇ are considered homogeneous. The uncertainty regarding the homogeneity studies was equivalent to $u_{\text{hom}} = 0.0034\%$. In addition, u_{hom} will be one of the sources of uncertainty for the CRM. The last uncertainty to be considered for certification of the candidate CRM is related to the uncertainty of characterization (u_{char}). Due to

Table 3. Analysis of variance for testing the homogeneity of the candidate CRM $K_2Cr_2O_7$, calculated with the coulometric titration data

Variation source	SS ^a	df ^b	MS ^c	F	P-value	F _{table}
Among	8.362×10^{-5}	2	4.181×10^{-5}	0.431	0.663	4.256
Within	8.733×10^{-4}	9	9.703×10^{-5}	–	–	–
Total	9.569×10^{-4}	11	–	–	–	–

^aSS: sums of squares; ^bdf: degrees of freedom; ^cMS: mean squares.

the high stability of the dichromate,¹⁴ the stability studies were not taken into account, therefore, the uncertainty of the stability of the CRM was considered null.

Characterization studies

The characterization of the candidate CRM, which will assign the value of the property certified for the CRM of $K_2Cr_2O_7$, was obtained by the mean results from seven replicates performed by precise constant-current coulometric titration. Table 4 shows the results of characterization of the candidate CRM of $K_2Cr_2O_7$, whose mean value for its purity, in a mass fraction, was equivalent to 99.97361%.

Table 5 illustrates the uncertainty budget, considering the GUM and EURACHEM/CITAC approach,^{25,26} for the coulometric characterization of the candidate CRM of $K_2Cr_2O_7$. The main contributions to the uncertainty evaluation were the current (66.0%), followed by the influence of the oxygen from the air in the coulometric cell (17.4%). The purity of the candidate CRM characterized by precise current-constant coulometric titration yielded the value of $99.9736\% \pm 0.0091\%$. This value is equivalent to (3.39833 ± 0.00031) mol kg⁻¹ as the amount content, for $k = 2$ with a coverage probability of approximately 95%.

Figure 4 shows the mean results for the characterization of the candidate CRM of $K_2Cr_2O_7$ by precise coulometric titration and their expanded uncertainties.

Table 5. Uncertainty budget for characterization of the candidate CRM of $K_2Cr_2O_7$

Source	Standard uncertainty, $u_i(x)$	Unit	Sensitivity coefficient, c_i	Uncertainty contribution, $u_i(v)$	Relative contribution, $u_i(v) / \%$
Repeatability	3.5×10^{-5}	mol kg ⁻¹	1	3.5×10^{-5}	5.2
Weighing	8.5×10^{-10}	kg	3.8×10^3	3.2×10^{-6}	0.04
Buoyancy correction	1.9×10^{-7}	1	43.4	8.3×10^{-6}	0.3
Time	8.7×10^{-7}	s	10.4	9.0×10^{-6}	0.33
Current	1.0×10^{-5}	A	12.2	1.2×10^{-4}	66.0
Faraday constant	5.8×10^{-5}	mol (A s) ⁻¹	1.5×10^{-1}	9.0×10^{-6}	0.33
End-point detection	1.4×10^{-5}	mol kg ⁻¹	1	1.4×10^{-5}	0.8
Chemical correction	2.6×10^{-5}	mol kg ⁻¹	1	2.6×10^{-5}	2.7
Incomplete rinsing	2.0×10^{-5}	mol kg ⁻¹	1	2.0×10^{-5}	1.6
Current efficiency	2.3×10^{-5}	mol kg ⁻¹	1	2.3×10^{-5}	2.1
Electrolyte impurities	2.0×10^{-5}	mol kg ⁻¹	1	2.0×10^{-5}	1.6
O ₂ influence	6.5×10^{-5}	mol kg ⁻¹	1	6.5×10^{-5}	17.4
Diffusion	2.0×10^{-5}	mol kg ⁻¹	1	2.0×10^{-5}	1.6
Combined uncertainty, $u_c(v)$	1.5×10^{-4}	mol kg ⁻¹			
Expanded uncertainty, $U(v)$	3.0×10^{-4}	mol kg ⁻¹	$k = 2; p = 95\%$		

Table 4. Characterization results of the candidate CRM of $K_2Cr_2O_7$

n ^a	Amount content / (mol kg ⁻¹)	Mass fraction / %
1	3.398417	99.97620
2	3.398426	99.97646
3	3.398339	99.97390
4	3.398201	99.96983
5	3.398278	99.97212
6	3.398412	99.97604
7	3.398230	99.97071
Mean	3.398329	99.97361
RSD ^b / %	0.003	0.003

^an: number of replicates; ^bRSD: relative standard deviation.

For the developed CRM of $K_2Cr_2O_7$, the combined standard uncertainty (u_c) of the CRM will be calculated by means of equation 1.

$$u_c = \sqrt{u_{hom}^2 + u_{char}^2} \quad (1)$$

The certification process for the candidate CRM of $K_2Cr_2O_7$ is completed with the evaluation of the uncertainty of the CRM. Taking into account the uncertainties related to the studies of homogeneity ($u_{hom} = 0.0034\%$) and characterization ($u_{char} = 0.0046\%$), the u_c of the CRM was

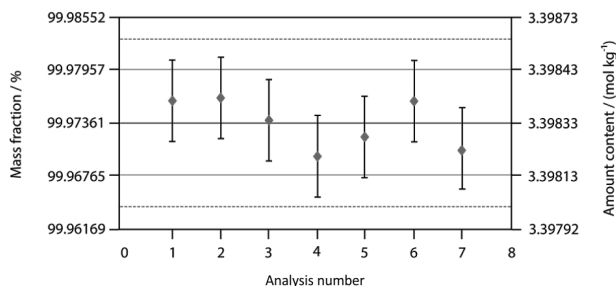


Figure 4. The measurement results for characterization of the candidate CRM of $K_2Cr_2O_7$. The solid line represents the certified value (mean from seven results), where each bar represents \pm the expanded uncertainty from the coulometric titration; the dashed lines represent the expanded uncertainty from the certified value, both for a coverage probability of approximately 95%.

equivalent to 0.0057%. Thus, the CRM of $K_2Cr_2O_7$ was certificated with the value $99.974\% \pm 0.011\%$ ($k = 2$, with a coverage probability of approximately 95%).

Monitoring studies were conducted in order to observe the stability of the material after its certification. Because it is a pure chemical solid compound, monitoring should verify whether the value of the certificate is confirmed in time, considering the limits of the expanded uncertainty from the certified material. According to the ISO Guide 35,⁹ inequality 2 is used for monitoring the CRM.

$$|x_{CRM} - x_{med}| \leq k \sqrt{u_{CRM}^2 + u_{med}^2} \quad (2)$$

where: x_{CRM} is the property value of the CRM; x_{med} is the observed value during the measurement; k is the coverage factor for coverage probability of 95%; u_{CRM} is the uncertainty of the CRM; and u_{med} is the uncertainty related to the measurement. In this case, if the material can be considered stable, both the property value and the expanded uncertainty are confirmed.

Table 6 illustrates the figure of merits for monitoring the CRM of $K_2Cr_2O_7$ by precise coulometric titration three months after it has been certified.

Table 6. Monitoring of the CRM of $K_2Cr_2O_7$

Monitoring	
Coulometric titration data	
x_{med} ($n = 3$)	99.96585%
u_{med}	0.0016%
CRM data	
x_{CRM}	99.9736%
$u_c = u_{CRM}$	0.0057%
Inequality	
$ x_{CRM} - x_{med} $	0.008%
$k \sqrt{u_{CRM}^2 + u_{med}^2}$	0.011%

Utilizing the data from Table 6, the results obtained confirm that the CRM continues to be stable, since the results from inequality 2 are true. It is worth noting that the monitoring of the batch of the CRM will continue every six months during its shelf life.

Conclusion

Both results from the bilateral comparison and CCQM-K96 for the assay of potassium dichromate by precise constant-current coulometric titration contributed to the reliability and experience in developing a CRM of potassium dichromate.

The candidate CRM of potassium dichromate was characterized by the PSC with a value of 99.9736% and an uncertainty characterization equivalent to $u_{char} = 0.0046\%$. The material was considered homogeneous by coulometry, with uncertainty $u_{hom} = 0.0034\%$. Thus, combining the uncertainties from the homogeneity and characterization studies, the CRM of $K_2Cr_2O_7$ was certified as $99.974\% \pm 0.011\%$, for $k = 2$ with a coverage probability of approximately 95%. On the other hand, the first monitoring of the CRM showed that the certified value was confirmed.

This CRM will contribute to ensuring the reliability and traceability of the measurement results that require potassium dichromate as a primary standard in redox titrations.

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