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COULOMETRIC DETERMINATION OF AMOUNT CONTENT OF POTASSIUM DICHROMATE FOR COMPARABILITY ASSESSMENT THROUGH A BILATERAL COMPARISON

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Abstract: A bilateral comparison between the National Metrology Institute (NMI) from Brazil (INMETRO) and Russia (UNIIM) for determining the amount content of potassium dichromate to assess the comparability of their measurements were performed. Samples of high purity potassium dichromate were exchanged and analysed by the INMs. The technique used was constant-current coulometry. Good comparability for one of the samples was obtained. After bias corrections in their measurements, both INMs will be able to certify reference materials of potassium dichromate that can be used for guaranteeing the quality of redox titrations in their countries.

Keywords: Primary standard, potassium dichromate, coulometric titration, certified reference materials.

1. INTRODUCTION

Coulometry is recommended as a potential primary method by the Consultative Committee for Amount of Substance-Metrology in Chemistry (CCQM) [1]. Coulometric determination of the amount of substance is directly linked with the mole, a base unit of the International System of Units (SI). Coulometry requires no reference for comparative evaluation and traceability. Coulometric methods are capable of high precision and accuracy. The NMIs use the coulometry to certify primary reference materials [2-6].

Certified reference materials (CRMs) are one of the most important products for guaranteeing the metrological traceability of measurements in chemical area. The CRMs determined by one of the primary methods of measurement are the highest element in the hierarchy of reference materials for composition of substances and materials.

The CRMs issued by the NMIs for being internationally accepted, the equivalence of the national traceability structures must be demonstrated on key comparison and pilot studies coordinated by CCQM [7].

Potassium dichromate ($K_2Cr_2O_7$) is recommended as a primary standard mainly for stoichiometric analysis by redox titration due to its extremely stability and easily-purified [8-9].

An international pilot comparison named CCQM-P7 was performed in 1999 for the assay of three primary standards including $K_2Cr_2O_7$. However, at that time, INMETRO, the NMI from Brazil, has not initiated its works in chemical metrology area yet.

For determining the amount content of the potassium dichromate, the NMIs from Brazil (INMETRO) and Russia (UNIIM) performed a bilateral comparison in order to assess the comparability of their results. In this bilateral comparison both primary systems of coulometry from each NMIs will be benchmarked for further development of CRM for oxidimetric analysis. An additional goal from this comparison can also be to check the protocols of measurement to help the INMs for the key-comparison denoted by CCQM-K96, which is currently been developed.

The aim of this work is to show the comparability results performed by the two NMIs on the analysis of $K_2Cr_2O_7$ through a bilateral comparison by using high accuracy constant-current coulometry.

2. MATERIALS AND METHODS

Two samples of high purity potassium dichromate were used for comparison: one sample provided by INMETRO (Brazil) and another by UNIIM (Russia). The NMIs exchanged both samples between each other. Each bottle of the sample contained approximately 30g of potassium dichromate. The mass fraction of potassium dichromate should be in the range from 99.5% to 100.0%. Each NMI was responsible for the homogeneity of their own samples. The method of measurement selected was coulometric titration with biamperometric end-point detection.

2.1 Method of Measurement: INMETRO

Two platinum electrodes compose the cell: the generation electrode (WE) made of a Pt plate with dimensions (5 cm × 6 cm × 0.04 cm) and the counter electrode (CE), a Pt plate (0.3 mm thickness) with 1 cm^2 area. An indicator electrode (IE) was used for end-point detection. It is made up of double platinum (Pt) electrode (two Pt wire of 1 mm diameter each). A potential of 0.050 V was applied between the two platinum wires. Before each measurement, the three electrodes (WE, CE and IE) were immersed for 10 min, firstly in a concentrated solution of potassium dichromate, and then plus 10 min in a solution of 0.2 mol L^{-1} ammonium iron(II) sulfate 6-water. The coulometric cell is made of glass. It has vertical design with two separate compartments.

The anodic compartment was filled with 2 mol L^{-1} H_2SO_4 and stays inside an intermediate compartment (IC) that is separated from the cathodic compartment through a silicate plug. This plug was prepared with silicate solution + 2 mol L^{-1} H_2SO_4 + water. The supporting electrolyte (250 mL) was a solution of 0.4 mol L^{-1} for ammonium iron(III) sulfate 12-water and 2 mol L^{-1} H_2SO_4. The coulometric cell was maintained at 23 °C during the assay by a thermostatic bath. The sample of potassium dichromate ($K_2Cr_2O_7$) was dried at 110 °C for 2 h, and cooled in desiccators over silica pellets. The current needed to the coulometric titration of $K_2Cr_2O_7$ sample was passed on 3 different phases: to the initial titration, a current of 4 mA; to the main titration a current of 300 mA and to the final titration, a current of 4 mA. Each sample of $K_2Cr_2O_7$ to be used for coulometric titration was weighed in the range of 500 mg by using a microbalance. All the weighing was corrected for buoyancy. Argon gas of high purity (99.999%) was passed through the cathodic compartment for deaeration or maintained above it during the titration phases. In all titrations the catholyte was stirred with magnetic stirrer. The end-point for each titration was calculated using linear regression using until eight points from the curve t (s) versus I (mA). At the start of each measurement, a volume of approximately 100-200 µL of 0.005 mol L^{-1} potassium dichromate was added to the supporting electrolyte to carry out the initial titration. Before the main titration, 15 min can be waited until the potassium dichromate sample is dissolved. The same supporting electrolyte was used in 6 replicates.

2.2 Method of Measurement: UNIIM

A vertical type cell consists of three compartments: working (cathodic), intermediate and auxiliary (anodic). Intermediate and auxiliary chambers have glass frites. In the anodic chamber, there is a silica gel plug that was prepared with 10 % sodium silicate solution + 2 mol L^{-1} H_2SO_4 + water. The catholyte was 0.4 mol L^{-1} Fe^{3+} (as ammonium iron(III) sulfate 12-water) in 2 mol L^{-1} H_2SO_4. The volume of the catholyte was 200 cm^3. The anolyte was 2 mol L^{-1} H_2SO_4., The volume of the anolyte was 100 cm^3. The generating cathode was a double Pt net (174 cm^2). The generating anode was a Pt net (87 cm^2). The indicating electrode has two Pt needles with diameter 0.5 mm and length 6mm.

The sample of potassium dichromate $K_2Cr_2O_7$ was dried at 110 °C for 2 h and cooled in the desiccator over phosphorous (V) oxide anhydrous. The generating and the indicating electrodes were treated by boiling concentrated nitric acid for 5 min, and then carefully rinsed by deionized water. After that, the Indicating electrode was immersed in the solution of potassium dichromate in H_2SO_4, then rinsed by water, and also stayed in Morh's salt ($(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$) solution and again rinsed by deionized water.

The catholyte was deaerated by argon (99.998 % purity) during 45 min as follows: the intermediate chamber for 5 min, then cathodic and anodic chambers for 40 min and also during the whole measurement. A solution containing 10 µL of 0.135 mol L^{-1} potassium dichromate was added. A little glass with $K_2Cr_2O_7$ to be assayed was located into the cell above the solution.

The initial titration was carried out using charge increments of 12 mA during·10 s. After each increment, the electrolyte from the intermediate chamber was pushed out and into by argon pressure. A PTFE spray shield above the solution was rinsed by immersing into the solution. The indicating current was measured by Picoammeter 6485. The value of the voltage applied to the needles of indicator electrode was 0.05 V. After indicating current increasing, the initial titration was carried out using charge increments of 12 mA·during 2 s. When initial titration is finished, the indicator electrode was located above the solution.

To determine the end point of the initial titration, the points before and after indicator current increasing were described by the linear equations using least-squares method.

The main titration was carried out using generating current of 160 mA. After the main titration, the intermediate chamber was rinsed as well as the spray shield. The $K_2Cr_2O_7$ to be assayed was put down to the solution. Then, final titration is carried out by a similar way as in the initial titration. All the weighing was corrected for buoyancy. Air temperature was maintained at 23 °C during the experiment by air conditioner. All titrations were carried out with the catholyte stirred with magnetic stirrer.

3. RESULTS AND DISCUSSION

Table 1 shows the measurement results of coulometric titration obtained by the two NMIs from the sample provided by UNIIM to the bilateral comparison. In this table the mean results of the amount content of potassium dichromate (mol kg^{-1}), combined standard uncertainty (u_C), relative combined standard uncertainty ($u_{C,r}$), relative standard deviation (RSD) and number of measurements (n) are reported.

Figure 1 presents the same measurement results in a graphical mode. It is worth to mention that the error bar considered was the expanded uncertainty of the measurement. This expanded uncertainty was obtained by the standard combined uncertainty multiplied by a coverage factor (k = 2), which represents approximately a 95% confidence level. As it can be seen in Figure 1, the results obtained by the two NMIs do not overlap. While the mean result from INMETRO was 3.396886 mol kg^{-1}, a mean result of 3.398256 mol kg^{-1} was obtained by the UNIIM. Even considering the mean or the weighted mean, the results showed no comparable for this sample. The bias should be corrected for obtaining comparability of the measurements.

Table 1- Measurement results of the bilateral comparison of the samples from UNIIM.

Institute	*Result /mol.kg^{-1}*	*$u_{C,}$ /mol.kg^{-1}*	*$u_{C,r}$*	*RSD*	*n*
INMETRO	3.396886	0.000168	0.005%	0.005%	8
UNIIM	3.398256	0.000319	0.009%	0.012%	9

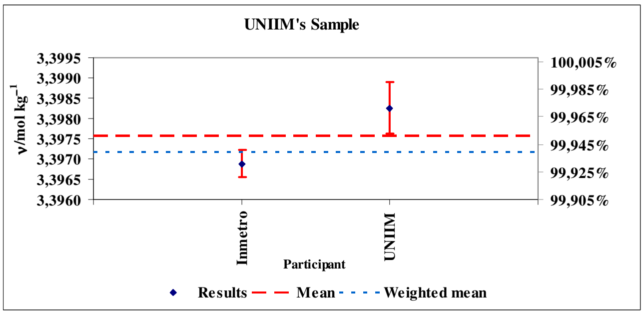

Figure 1- Results from UNIIM's sample. The dashed lines represent the mean value (in red) and the weighted mean (in blue). Error bars correspond to expanded uncertainties, *k*=2, for a confidence level of approximately 95%. The mass fractions of the potassium dichromate that correspond to the amount content can be seen on the right side (secondary axis).

As for the sample from INMETRO, the results performed by the two NMIs are presented in Table 2. In this table the mean results of the amount content of potassium dichromate (mol kg^{-1}), combined standard uncertainty (u_C), relative combined standard uncertainty ($u_{C,r}$), relative standard deviation (RSD) and number of measurements (n) are reported. Graphically, the same results are shown in Figure 2. These results were considered comparable due to the uncertainty of the measurements according to GUM [10]. The main uncertainty sources considered by INMETRO were: weighing, buoyancy correction, time, current, Faraday constant, end-point determination, chemical corrections, incomplete rising, current efficiency, electrolyte impurities, oxygen influence, diffusion.

Table 2- Measurement results of the bilateral comparison of the samples from INMETRO.

Institute	***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

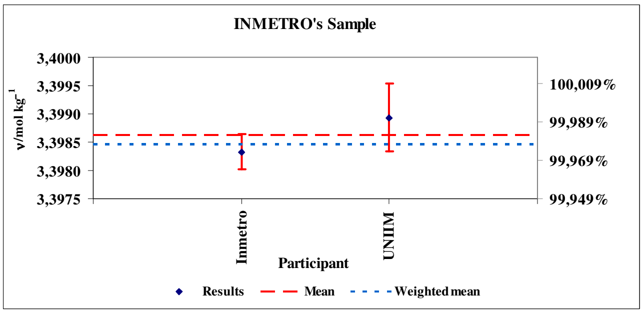

Figure 2- Results from INMETRO's sample. The dashed lines represent the mean value (in red) and the weighted mean (in blue). Error bars correspond to expanded uncertainties, *k*=2, for a confidence level of approximately 95%. The mass fractions of the potassium dichromate that correspond to the amount content can be seen on the right side (secondary axis).

3. CONCLUSIONS

The results between the two NMIs for the assay of potassium dichromate by coulometric titration showed good performance. The main goal of this comparison, which was the comparability of the measurement, was reached, though the results from one of the samples did not overlap. Therefore, with the improvement of the methodology and corrections of the bias on their measurements, both NMIs will be able to participate in the key comparison on the frame of CCQM for the assay of potassium dichromate, as well as to develop CRM of potassium dichromate to guarantee the traceability and reliability of the stoichiometric analysis by redox titration in their countries.

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