Potassium calibration solution: production and certification at Inmetro

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Abstract. MRC 8757.0001, a single-element potassium calibration solution, was prepared and certified at Inmetro. The Certified Reference Material (CRM) was gravimetrically prepared with an internally certified high-purity potassium chloride in an acidified aqueous solution. The batch consisted of 152 units, packed in a 125 mL capped polypropylene bottle, protected with a polypropylene bag and an aluminized pouch. Certification studies were performed according to ISO GUIDE 35, ISO 17034 and internal standards. High-Performance Inductively Coupled Plasma Optical Emission Spectrometry (HP ICP OES) was applied as a measurement method. The certified potassium mass fraction was 1002 mg/kg, with an expanded uncertainty of 11 mg/kg, considering a coverage factor of k = 2.02 for a confidence level of approximately 95 %. With HP ICP OES we improved the production and certification of calibration solutions by diminishing the expanded uncertainty of MRC 8757.0001 to up to 47 %, when compared to another calibration solution prepared at Inmetro.

Keywords: calibration solution, HP ICP OES, measurement uncertainty, traceability, certified reference material.

1. Introduction

Calibration solutions are a specific type of CRMs that provide the basis of quantitation for inorganic analysis and for most of instrumental techniques [1], such as Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). These CRMs are used by chemical analysis laboratories to calibrate their instruments, and also to provide accuracy, reliability and metrological traceability to their measurement results, especially if the laboratory is accredited or seeking ISO 17025 accreditation. In order to attend to the needs of chemical laboratories for metrological traceability, and also to support the objective from the National Institute of Metrology, Quality and Technology (Inmetro) to provide technological solutions and quality infrastructure for the productive sector [2], the Inorganic Analysis Laboratory (Labin), from the Chemical Metrology Department at Inmetro is producing and certifying calibration solutions [3].

External calibration [4] has been used for certification studies or characterization of property values for calibration solutions. HP ICP OES is a measurement method consisting in an element specific "two-pan balance" combined with a drift correction procedure, which allows performance comparable to isotope dilution and classical methods [5]. The method has been applied by National Metrology Institutes for certification processes of single-element calibration solutions [6,7].The potential of HP ICP OES was already identified as a characterization strategy for calibration solutions at Inmetro, when compared to other analytical methods [8], nevertheless, it was not fully applied as a measurement method for all the stages of a certification process [9].

In this work we present the results for homogeneity assessment, as well as short-term and long-term stability assessment and characterization for MRC 8757.0001, a potassium single-element calibration solution. The CRM was produced and certified following ISO 17034 [10], ISO GUIDE 35 [11] and Inmetro's internal standards. Furthermore, we present the improvements that HP ICP OES has provided when used as a measurement method for certification studies of calibration solutions prepared at Inmetro.

2. Methods and calculations

The batch was gravimetrically prepared by dissolving KCl-Inmetro-1, a potassium chloride salt internally assessed for purity at Inmetro [12], in an aqueous acidified matrix (HNO_3 3 %). Each CRM unit (n = 152) contains approximately 100 mL of solution, packed in a 125 mL capped polypropylene bottle, protected with a polypropylene bag and an aluminized pouch.

Homogeneity assessment was performed using a measurement in a single run design. Short-term stability (transport condition) was assessed using an isochronous design, by studying the effects of temperature (50 °C) on the potassium mass fraction, for 0, 5, 12, 19, 24 or 31 days. Long-term stability was assessed using a classical design and studying the potassium mass fraction in storage conditions (20 °C – 25 °C) for 188, 371, 412, 450, 476, 507 and 538 days after preparation. The effect for repeated sampling was also assessed by analyzing the same unit throughout all of the certification studies.

Analysis of variance (Anova) and linear regression analysis were the statistical approaches applied for homogeneity and stability assessments (short-term, long-term and repeated sampling), respectively. Stratified random sampling was used for sample selection in all of the aforementioned studies.

The mass fraction (mg/kg) characterization of potassium was made using the formulation method and HP ICP OES as a confirmation method. KCl-Inmetro-2, a potassium chloride salt assessed for purity at Inmetro [12], was used to prepare the internally certified calibration solutions (calibrants). SRM 999b (NIST) was used for accuracy assessment.

HP ICP OES analysis were performed for all the aforementioned certification studies on an ICP OES Optima 8300 (Perkin Elmer) equipped with a Scott chamber, a cross-flow nebulizer and a S10 autosampler. ICP OES conditions were a plasma, auxiliary, nebulizer and pump flow rates of 12 L/min, 0.5 L/min, 0.9 L/min and 1.0 mL/min, respectively, with an axial view and 1100 W. Data was acquired using peak area, 5 points per peak, an integration time of 0.010 s and a read time of 8.0 s. Potassium, K (3.6 mg/kg), was detected at 766 nm. Strontium, Sr (0.17 mg/kg) was used as an internal standard and was detected at 407 nm. All samples were prepared and dilluted gravimetrically in duplicate, with a mass deviation lesser than 0.3% of the target mass fractions. Analysis were performed using 5 runs of randomized measurements, alternating a calibrant and a sample or a control solution.

Homogeneity standard uncertainty, u_h, was calculated using Anova results and equation 1, in which MQ_B is the between-group mean square, MQ_w is the within-group mean square and n is the number of samples.

$$u_h = [(MQ_B - MQ_w)/n]^{1/2} \qquad (1)$$

Short-term and long-term stability standard uncertainties, u_{its}, were each calculated according to equation 2, in which s_b is the slope error of a linear regression model, and T is the duration of the study, in days.

$$u_{its} = s_b \text{ x } T \tag{2}$$

The combined standard uncertainty (u_c) was calculated using equation 3, in which u_h is the homogeneity standard uncertainty, u_{ch} is the characterization standard uncertainty, u_{lts} is the long-term stability standard uncertainty (storage conditions) and u_{sts} is the short-term standard uncertainty (transport conditions). Degrees of freedom were calculated using equation 4, in which gl denotes a degree of freedom, and the subindex denotes one of the aforementioned studies.

$$u_c = [u^2_h + u^2_{ch} + u^2_{lts} + u^2_{sts}]^{1/2} \tag{3}$$

$$gl = u^4_c/[u^4_h/gl_h + u^4_{ch}/gl_{ch} + u^4_{lts}/gl_{lts} + u^4_{sts}/gl_{sts}\ ] \tag{4}$$

The potassium mass fraction obtained from the formulation method, x_G, (gravimetric preparation) was compared with the one obtained with HP ICP OES, x_{HP} using equation 5.

$$|x_G\text{-}x_{HP}| \leq 2 \times [u^2_{xG} + u^2_{xHP}]^{1/2} \tag{5}$$

3. Results

The assessment, evaluation criteria and standard uncertainty results obtained for homogeneity and stability studies are summarized in table 1. For homogeneity assessment, a p-value of 0.11 for the within-group variation showed that the batch was homogeneous.

For stability studies, a linear regression model was constructed with the duration of the study (days) under de assessed temperature (20 °C – 25 °C, or 50 °C) as the independent variable, and the potassium mass fraction as the dependent variable. A non-significant slope of each model was used as a stability criterion. For both short-term stability (p-value of 0.21) and long-term stability studies (p-value of 0.09), that criterion was achieved.

Table 1. Certification studies assessment for MRC 8757.0001

Certification study	Statistical assessment	Evaluation criteria	u_i, %
Homogeneity	Anova	Non-significant within group variation (p-value > 0.05)	0.23
Short-term stability (transport conditions, 50 °C)	Linear regression	Non-significant slope (p-value > 0.05)	0.37
Long-term stability (storage conditions, 20 °C – 25 °C)			0.24

The repeated sampling of the same MRC 8757.0001 unit kept under storage conditions (20 °C – 25 °C), was evaluated also with a linear regression model in which the variability of the potassium mass fraction (mg/kg) was assessed over time (days). A non-significant slope (p-value of 0.18) was also obtained. Since the standard uncertainty for long-term stability was already accounted for, we did not considered the repeated sampling standard uncertainty for the combined standard uncertainty calculation.

As a characteristic of HP ICP OES, with every certification study (homogeneity or stabilities), a potassium mass fraction of the batch was obtained. Thus, the mean of these values (1003.2 mg/kg) and their standard uncertainty (1.9 mg/kg), were compared with the mass fraction obtained using the formulation method (1000.587 mg/kg) and its standard uncertainty (0.034 mg/kg) using equation 5. The difference between the absolute value of both mass fractions (2.6 mg/kg) was lesser than their combined standard uncertainty (4.2 mg/kg) multiplied by a coverage factor, (k = 2.18, 12 degrees of freedom and a 95 % confidence level), therefore there was a non-significant difference between both results. According to ISO GUIDE 35, this purely gravimetric value is sufficient for value assignment, nevertheless, we preferred to use a more conservative approach and used both results. The characterized potassium mass fraction (1001.9 mg/kg) was calculated using the mean of the gravimetric and HP ICP OES mass fractions. The characterization standard uncertainty was calculated using the square root of the quadratic sum of the gravimetric and HP ICP OES standard uncertainties. The relative characterization standard uncertainty was 0.19%.

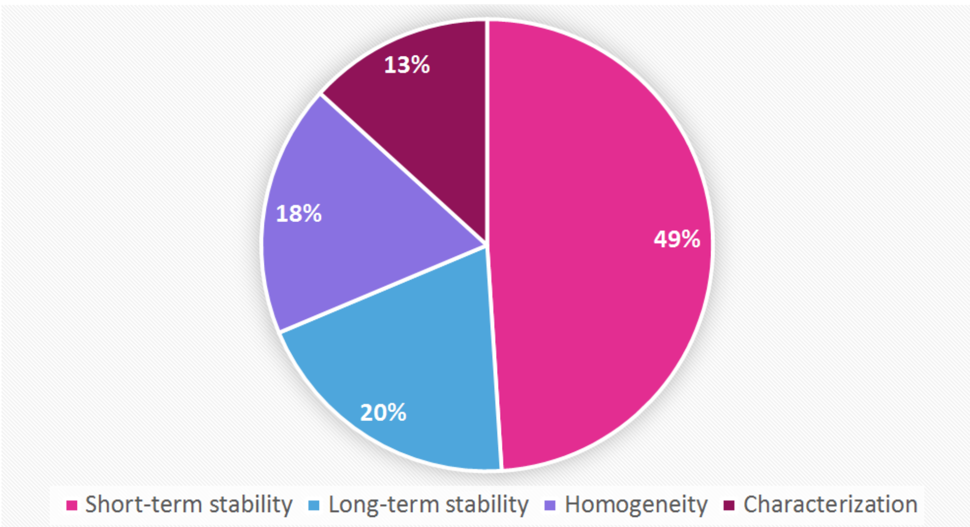
The results for all of the certification studies of MRC 8757.0001: homogeneity, short-term stability, long-term stability and characterization are summarized in Table 2.

Table 2. Certification studies standard uncertainties for MRC 8757.0001

Certification study	Standard uncertainty	Degrees of freedom
Homogeneity	2.3 mg/kg	40
Short-term stability (transport, 50 °C)	3.7 mg/kg	10
Long-term stability (storage, 20 C – 25 °C)	2.4 mg/kg	43
Characterization	1.9 mg/kg	--
Combined standard uncertainty	5.3 mg/kg	38

In Figure 1 we present the relative contribution of each certification study, expressed as $(u_i/u_c)^2$, where u_i is the standard uncertainty of the certification study i and u_c is the combined standard uncertainty. In that Figure, short-term stability was the main source of contribution for the combined standard uncertainty.

Figure 1. MRC 8757.0001 relative standard uncertainties, expressed $(u_i/u_c)^2$



Using the characterization, homogeneity and short-term and long-term stability standard uncertainties (table 2), and the equations provided in Section 2, the relative combined standard uncertainty for the potassium calibration solution was 0.53 %. With these results and using HP ICP OES, we obtained a reduction of 47 % , when compared with the relative combined standard uncertainty (1.13 %) of another calibration solution also prepared at Labin, but using external calibration as a measurement method for homogeneity, short-term and long term stability [9]. Therefore, HP ICP OES proved to be a more efficient measurement method than external calibration for certification studies in calibration solutions. Additionally, this result also shows that the single-element calibration solution production and certification process at Labin is being furtherly refined and improved.

Considering the aforementioned results, the certified mass fraction of the MRC 8757.0001 (Figure 2) was 1002 mg/kg, with an expanded uncertainty of 11 mg/kg, considering a coverage factor of $k = 2.02$ for a confidence level of approximately 95 % [13].

Figure 2. MRC 8757.0001 Potassium calibration solution

4. Conclusions

MRC 8757.0001, a potassium calibration solution, was adequately prepared and certified at Inmetro according to ISO 17034, ISO Guide 35 and internal standards. The CRM is homogeneous and stable under transportation (50 °C) and storage (20 °C – 25 °C) conditions, and can be sampled repeatedly. The certified mass fraction was 1002 mg/kg, with an expanded uncertainty of 11 mg/kg, considering a coverage factor of $k = 2.02$ and a confidence level of approximately 95 %.

The usage of HP ICP OES as a measurement method for certification studies proved to be more efficient than external calibration, allowing to decrease the expanded uncertainty of MRC 8757.0001 and proving that the production and certification of calibration solutions at Labin is being improved.

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