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Research Article

Uncertainty Estimation for Determination of Potassium Iodate Purity by Potentiometric Titrimetry

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Abstract

The purpose of this study was to express the uncertainty estimation for the purity determination of potassium iodate by potentiometric titrimetry method. Potassium iodate determination by using a potentiometric titrator was realized in two steps. In the first step, a factor analysis was performed using sodium thiosulfate. In the second step, the amount of potassium iodate was determined by using the factor value obtained in the first step of the measurement. Sigma Aldrich 60386 CRM (certified by BAM-with purity of 99.94%) was used for factor analysis. The documents of "Evaluation of measurement data - Guide to the expression of uncertainty in measurement" and "EA-4/02 M: 2013 Evaluation of the Uncertainty of Measurement in Calibration" were the source for the evaluation of the measurement uncertainty. The documents of "EURACHEM/CITAC Guide CG 4, JCGM 100: 2008" and "Eurolab Technical Report No.1/2007" based on the bottom-up approach were also paid regard during the uncertainty estimation study. The main factors that are forming the total uncertainty budget were repeatability of the measurement results, titrant consumption, factor of sodium thiosulfate, the molar mass of potassium iodate and sample quantity. It was observed that the highest contribution to the uncertainty budget was the repeatability of measurement results. The measurement result for the purity determination of potassium iodate was found as 99.76% and the expanded uncertainty of the measurements was estimated as 0.12% which was acceptable level for the study.

Keywords: Potentiometry, titrimetry, potassium iodate, measurement uncertainty, bottom-up approach.

Potasyum İyodatın Saflığının Potansiyometrik Titrimetri ile Belirlenmesi için Belirsizlik Hesaplanması

Öz

Bu çalışmanın amacı, potansiyometrik titrimetri yöntemi ile potasyum iyodatın saflık tayini için belirsizlik hesaplamasının ifade edilmesidir. Potasyum iyodat tayini, potansiyometrik titratör kullanılarak iki aşamada gerçekleştirilmiştir. İlk aşamada, sodyum tiyosülfat kullanılarak bir faktör analizi gerçekleştirilmiştir. İkinci aşamada ise, ölçümün ilk aşamasında elde edilen faktör değeri kullanılarak potasyum iyodat miktarı belirlenmiştir. Faktör analizi için Sigma Aldrich 60386 CRM (BAM sertifikalı-% 99,94 saflıkta) kullanılmıştır. Ölçüm belirsizliğinin değerlendirilmesi sırasında, "Ölçüm verilerinin değerlendirilmesi - Ölçüm belirsizliğinin ifade edilmesi kılavuzu" ve "EA-4/02 M: 2013 Kalibrasyonda Ölçüm Belirsizliğinin Değerlendirilmesi" dokümanlarından kaynak olarak yararlanılmıştır. Aşağıdan yukarıya yaklaşıma dayalı "EURACHEM / CITAC Kılavuzu CG 4, JCGM 100: 2008" ve "Eurolab Teknik Raporu No. 1/2007" de belirsizlik tahmin çalışması sırasında dikkate alındı. Toplam belirsizlik bütçesini oluşturan ana faktörler, ölçüm sonuçlarının tekrarlanabilirliği, titrant tüketimi, sodyum tiyosülfatın faktörü, potasyum iyodatın molar kütlesi ve numune miktarıdır. Belirsizlik bütçesine en yüksek katkının ölçüm sonuçlarının tekrarlanabilirliği olduğu gözlemlenmiştir. Potasyum iyodatın saflık tayini için ölçüm sonucu % 99,76 olarak bulunmuş ve ölçümlerin genişletilmiş belirsizliği % 0,12 olarak çalışma için kabul edilebilir bir düzey olarak hesaplanmıştır.

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Anahtar Kelimeler: Potansiyometri, titrimetri, potasyum iyodat, ölçüm belirsizliği, aşağıdan yukarıya yaklaşımı

1. Introduction

Potassium iodate (KIO_3) is a significant chemical for the volumetric, coulometric or potentiometric analysis for titration of some ions such as $S_2O_3^{2-}$, As^{3+}, Fe^{2+}, I^-, Sn^{2+}, SO_3^{2-} etc. KIO_3 is preferred in production of certified reference material due to its easy purification and long term stability (Hulanicki et al., 2013). Due to these properties of KIO_3, it has been produced and certified as a primary standard especially for oxidation-reduction processes (Tuthill et al., 1996).

When the literature is investigated it can be seen that there are some studies for the determination of KIO_3. Most of the studies were based on the method of potassium iodate titration by sodium thiosulfate which were standardized by potassium dichromate solution by using volumetric or coulometric measurement methods. These well-known methods were also used by national metrology institutes for the production of certified reference materials (CRMs) (Shimolin et al., 2017; Mariassy et al., 2009; Asakai et al., 2007). In addition to these, potentiometric tirimetry, another type of volumetric titrimetry, was also used in such purity determinations due to being simple, cheap, fast and easy-to-use (Liv, 2021).

In principle, a potentiometric titration is a chemical analysis method based on the measurement of a potential difference between two electrodes in order to determine the concentration of an analyte. This method is a type of volumetric titration method in which a reference electrode and an indicator electrode are included. The endpoint of a titration is monitored by the indicator electrode that measures the potential change as a function of the volume of the added titrant of exact concentration against the reference electrode. In this method, the obtained titration curve provides more information to the user than the classical method. It also gives data such as the curve shape, position, time throughout the measurement process.

There are different application kinds of the potentiometric titrations for the characterization of analytes in varied solutions such as acid/base, redox, precipitation, and complexometric analysis. The main advantages of the potentiometric titrations when compared to the manual titrations, it can be observed that they are more practical. In addition, the potentiometric titrations have higher accuracy and precision. Another advantage of this method is that it is suitable for working with small amount of samples. It is also an inexpensive method in terms of device, infrastructure and apparatus (Ma, 2002).

Titrimetric determination of potassium iodate is carried out in two steps. The first step is the standardization of sodium thiosulfate in which a factor is determined in order to use in the calculation in the next step of the measurement. The second step is the titration of potassium iodate.

Reaction steps for the analysis are shown in the following reactions:

$$IO^{3-} + 5I^{-} + 6H^{+} \rightarrow 3I_2 + 3H_2O \qquad (1)$$

$$2S_2O_3^{2-} + I_2 \rightarrow 2I^{-} + S_4O_6^{2-} \qquad (2)$$

Temperature is another significant factor for this kind of analysis which was constant during the process.

The measurement uncertainty is perhaps the most important thing of the typical issues in purity analysis. In addition to the purity value aimed to be measured, the uncertainty value expressing the distribution of the expressed values is also a notifier of the accuracy of the measurement. In the evaluation of measurement uncertainty, the documents "Evaluation of measurement data - Guide to the expression of measurement uncertainty" and "EA-4/02 M: 2013 Evaluation of Measurement Uncertainty in Calibration" have been used as references. As a further matter, the other main uncertainty approaches named as bottom-up approach are the approaches that evaluate the effect of each component on total uncertainty in a systematic and detailed manner. This approach is modelled in terms of the explanations in EURACHEM/CITAC Guide CG 4, JCGM 100: 2008 and Eurolab Technical Report No.1/2007.

In this study that was realised in TUBITAK UME Electrochemistry Laboratory, it was targeted to establish an uncertainty budget which was not found in the literature for determination of potassium iodate purity by potentiometric titrimetry with details and also to prove the method accuracy. To the best of our knowledge, there is no detailed measurement uncertainty study based on the bottom-up approach and potentiometric titrimetry for the purity determination of potassium iodate.

2. Material and Methods

2.1. *Chemicals*

Sodium thiosulfate ($Na_2S_2O_3$), potassium iodide (KI), potassium iodate (KIO_3) and sulfuric acid (H_2SO_4) were obtained from Merck at Emsure level.

Certified Potassium iodate (Sigma Aldrich 60386) CRM (certified by BAM with a purity of 99.94%) was used for the factor analysis.

2.2. *Apparatus*

Metrohm 916 Ti-touch auto-titration system with a platinum titrode (6.0431.100) electrode was used in the measurements.

Milli-Q Integral 10 water purification system was used to produce ultrapure water (18.2 MΩ.cm (at 25°C)) for sample preparation and cleaning.

During the sample preparation processes before the measurements, HDPE (High Density Polyethylene) bottles were used.

Precisa LS 220A analytical balance was used for weighing operations for the sample preparation.

2.3. *Measurement Procedure*

Approximately 300 mg of KIO_3 was weighed in a clean beaker and 150 mL of deionized water was added into the beaker. Then approximately 1.7 g KI and 10 mL of H_2SO_4 were added into the mixture. This solution was homogenised by hand mixing. Iodine (I_2) released after homogenisation was titrated potentiometrically with standardised sodium thiosulfate ($Na_2S_2O_3$) solution automatically.

This step is called as "Standardisation of $Na_2S_2O_3$" or in other words "Factor Analysis" and the factor is obtained at the end of this step.

$$Na_2S_2O_{3_{factor}} = \frac{C_{00} \times 600}{M \times V \times C} \qquad (3)$$

In this equation, C_{00} is the sample quantity (g), 600 is the correction factor, C is the nominal concentration of the titrant (0.1 mol/L), M is the molar mass of KIO_3 (214.001 g/mol) and V is the titrant consumption (mL).

In the second step, the process performed in the first stage was repeated exactly in the same way. At the end of the analysis, the purity of KIO_3 was determined.

$$Purity(\%) = \frac{V \times F \times C \times M}{600 \times C_{00}} X100 \qquad (4)$$

In this equation, F is the factor value of $Na_2S_2O_3$ titration, V is the titrant consumption (mL), 600 is the correction factor, M is the molar mass (214.001 g/mol) and C is the nominal concentration of the titrant (0.1 mol/L) and C_{00} is the sample quantity (mg).

2.4. *Evaluation of Measurement Uncertainty*

The guides and standard documents used during the evaluation of the measurement uncertainty were explained in the "Introduction" section. As an additional information; the expanded uncertainties were obtained by multiplying the combined uncertainties by 2 as a coverage factor, at 95% confidence level.

3. Results and Discussion

3.1. *Standardisation of $Na_2S_2O_3$*

For the factor determination, the measurements were repeated for 5 different samples prepared from the certified reference material. The results of the measurements for each sample are demonstrated in Table 1.

After the measurements were performed, the average of the factors was calculated as 1.0066.

Table 1. The measurement results of factor determination

Replicate	Weighed KIO_3 (g)	Weighed KI (g)	Added Titrant (mL)	Temperature (°C)	Factor
1	0.3185	1.6608	150	49.0	1.0057
2	0.3274	1.6553	150	48.7	1.0044
3	0.3359	1.6519	150	48.3	1.0063
4	0.3251	1.6550	150	49.0	1.0073
5	0.3235	1.6512	150	49.9	1.0094
				$\bar{x}$	1.0066
				s	0.0008

3.2. *Purity determination of potassium iodate*

The results of the purity determination of potassium iodate are shown in Table 2. The fishbone diagram for the purity determination of potassium iodate is shown in Fig. 1.

Table 2. The measurement results of purity determination of potassium iodate

Replicate	Weighed KIO_3 (g)	Weighed KI (g)	Added Titrant (mL)	Calculated KIO_3 (g)	Titrant Consumption (mL)	Purity of KIO_3 (%)
1	0.3390	1.6532	150	0.3378	9.4197	99.76
2	0.3332	1.6506	150	0.3317	9.2464	99.63
3	0.3405	1.6509	150	0.3397	9.4688	99.84
4	0.3623	1.6507	150	0.3618	10.0857	99.95
5	0.3365	1.6537	150	0.3350	9.3369	99.62
					$\bar{x}$	99.76
					s	0.14

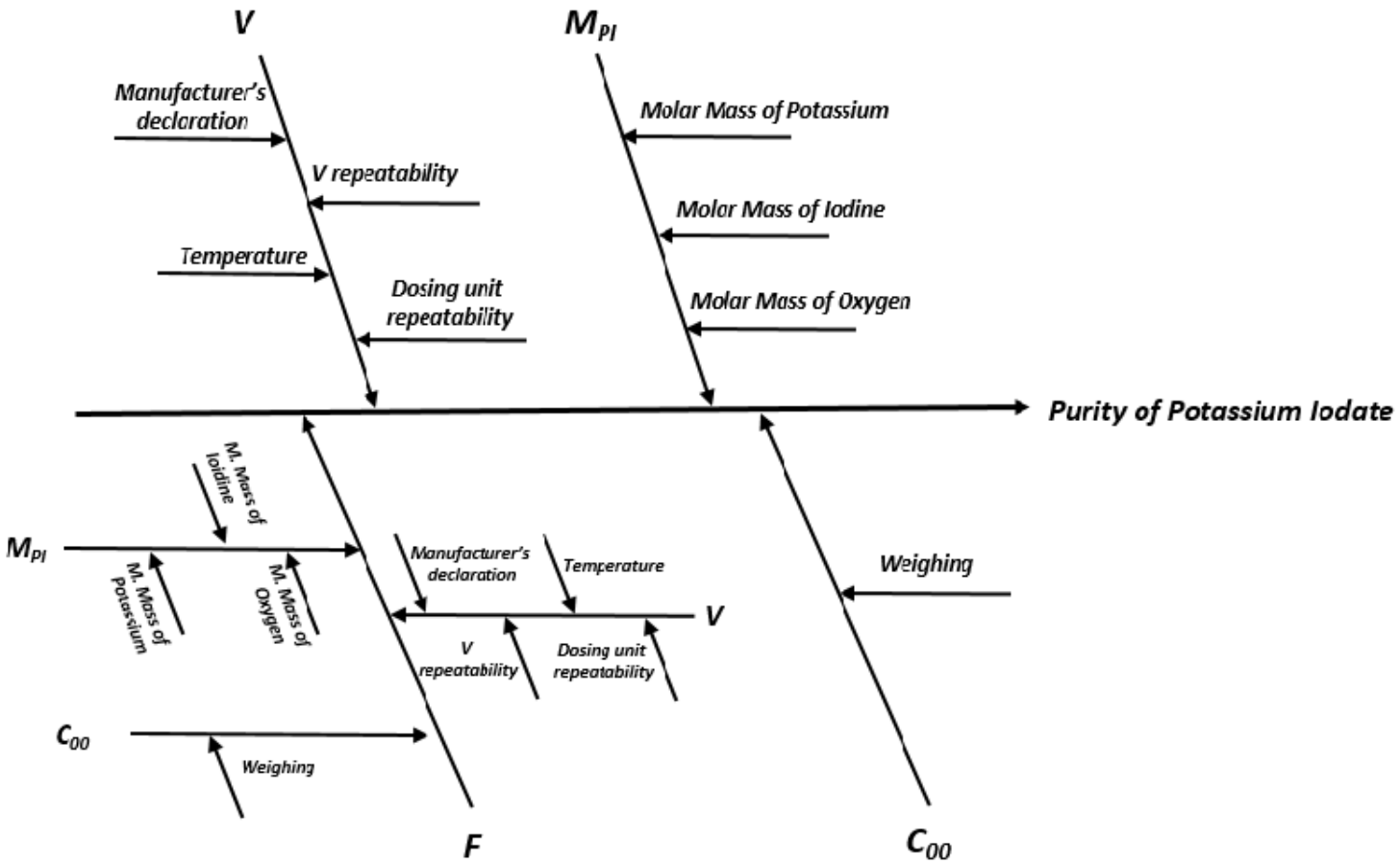

Figure 1. The fishbone diagram for the purity determination of potassium iodate

3.3. *Measurement Uncertainties*

The documents named as “Evaluation of measurement data - Guide to the expression of uncertainty in measurement” and “EA-4/02 M: 2013 Evaluation of the Uncertainty of Measurement in Calibration” were the source guides for evaluation of the uncertainty budget. “EURACHEM/CITAC Guide CG 4, JCGM 100: 2008” and “Eurolab Technical Report No.1/2007” were also paid regard during the uncertainty estimation study. The sensitivity coefficients used in the uncertainty budgets were also determined in terms of the approaches defined in these guides.

3.3.1 *Evaluation of the Uncertainty Budget for Factor Analysis*

The standard uncertainty of $F_{Na_2S_2O_3}$ is calculated as a combination of four different standard uncertainties: the titrant consumption, the molar mass of potassium iodate, sample amount of certified KIO_3 and $F_{Na_2S_2O_3}$ repeatability. All the standard uncertainties of these different sources were calculated as Liv performed in his work (Liv (2021)). The details of the uncertainty budget were shown in Table 3.

Table 3. Uncertainty budget for factor analysis

Inputs				Uncertainty Component								
Symbol	**Definition**	**Estimated Value (x_i)**		**Value**		**Probability distribution**	**Multiplier**	**Standard Uncertainty $u(x_i)$**		**Sensitivity Coefficient (c_i)**		**Contribution to Uncertainty**
F	Factor	1.0066	-	0.0008	-	Normal	1	0.0008	-	1		0.0008
V	Titrant Consumption	9.0823	mL	0.0815	mL	Normal	1	0.0815	mL	-0.0001	1/mL	0.00001
M	Molar Mass	214.001	$g.mol^{-1}$	0.0006	$g.mol^{-1}$	Rectangular	1	0.0006	$g.mol^{-1}$	-4.7×10^{-6}	$mol.g^{-1}$	2.85×10^{-9}
Coo	Sample Quantity	0.32608	g	0.0029	g	Normal	1	0.0029	g	0.0031	g^{-1}	8.9×10^{-6}
F	**Factor**	**1.0066**								**Combined Uncertainty $u(y)$**		0.0008
										Expanded Uncertainty $U(y)$ (k=2)		**0.0017**
										% Expanded Uncertainty $U(y)$% (k=2)		**0.17**

3.3.2 *Evaluation of the Uncertainty Budget for Purity of Potassium Iodate*

In terms of evaluation of the practical results of the measurements performed at TUBITAK UME, the components of the uncertainty budget are the standard uncertainties derived from the factor value, the titrant consumption, the molar mass, the nominal concentration of the titrant and sample quantity. The standard uncertainty of V was determined by dividing the standard deviation of 5 different titrant consumption values to square root of the sampling number ($\sqrt{5}$). After that, the total uncertainty of the titrant consumption was calculated by combining the standard uncertainty, temperature effect and the values from the company declaration.

The standard uncertainty of the repeatability was evaluated by dividing the standard deviation of five replicates from the purity determination of potassium iodate to the square root of replicate numbers ($\sqrt{5}$). The standard uncertainty of sample quantity was evaluated by combination of both analytical balance operation and sample weighing operations. The standard deviation of five different sample weighing operations was divided by the square root of the sample numbers ($\sqrt{5}$).

The standard uncertainty of analytical balance operation was calculated according to the expanded uncertainty value of the calibration certificate of the analytical balance.

The standard uncertainty of the molar mass of potassium iodate was evaluated according to the IUPAC (Van der Veen, 2016) and CIAAW (CIAAW, 2018) recommendations. The standard atomic weights of each element (2 values for each element) were summed up. Then this value was divided by 2 to calculate the average mass of potassium iodate. The standard uncertainties of mass (u_{s,W_i}) were calculated according the Eq 5.

$$u_{s,W_i} = \frac{|w_{i,1} - w_{i,2}|}{2\sqrt{3}} \qquad (5)$$

The uncertainty contribution of each element was found by multiplying u_{s,W_i} by the stoichiometric coefficient and the standard uncertainty of the molar mass of potassium iodate ($u_{s,W_{PI}}$) was calculated as 0.0006 g.mol^{-1} by taking the square root of the sum of squares of each uncertainty contribution. The calculation for the standard uncertainty of molecular weight of potassium iodate is shown in Table 4.

Table 4. The calculation of standard uncertainty of molecular weight of potassium iodate (u_{s,W_i})

Component	Standard atomic weight (w_i)	Probability distribution	Average mass	Standard uncertainty of mass (u_{s,W_i})	Stoichiometric coefficient	Uncertainty contribution
K	[39.0983]	Rectangular	39.0983	0.000001	1	0.000001
I	[126.90447]	Rectangular	126.90447	0.000003	1	0.000003
O	[15.99903, 15.99973]	Rectangular	15.99938	0.000202	3	0.000606
KIO_3			214.001			0.0006

The expanded uncertainty of the determination of potassium iodate purity was evaluated by combining all the standard uncertainty sources and obtained by expanding the combined value by multiplying by the coverage factor which is 2. Finally, the result of the purity determination was reported as (99.76 ± 0.12)%, (*k=2*), at 95% confidence level.

The uncertainty level was determined approximately 0.12%. As shown in Figure 2, the highest contribution to the measurement uncertainty was derived from the repeatability. But it should be mentioned that the effect of the sample quantity and the titrant consumption cannot be ignored out of consideration if taking a glance at the numerical values in the uncertainty contributions in Table 5.

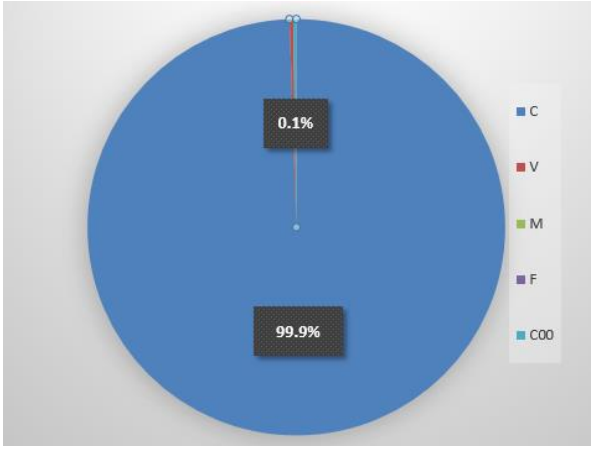

Figure 2. The contributions to the measurement uncertainty

The uncertainty budget of the measurements for the purity determination of potassium iodate is shown in Table 5.

Table 5. Uncertainty budget of purity measurement of potassium iodate

Inputs				Uncertainty Component								
Symbol	**Definition**	**Estimated Value (x_i)**		**Value**		**Probability distribution**	**Multiplier**	**Standard Uncertainty $u(x_i)$**		**Sensitivity Coefficient (c_i)**		**Contribution to Uncertainty**
C	Repeatability	99.76	-	0.0622	-	Normal	1	0.0622	-	1		0.0622
V	Titrant Consumption	9.5115	mL	0.1487	mL	Normal	1	0.1487	mL	0.0012	1/mL	0.0002
M	Molar Mass	214.001	$g.mol^{-1}$	0.0006	$g.mol^{-1}$	Rectangular	1	0.0006	$g.mol^{-1}$	5.46×10^{-6}	$mol.g^{-1}$	3.28×10^{-9}
F	Factor	1.0066	-	0.0008	-	Normal	1	0.0008	-	1.16×10^{-3}	-	9.29×10^{-7}
Coo	Sample Quantity	0.3423	g	0.0051	g	Normal	1	0.0051	g	-2.91×10^{-2}	g^{-1}	0.00015
%P	**Purity**	**99.76**								**Combined Uncertainty $u(y)$**		0.06
										Expanded Uncertainty $U(y)$ (k=2)		**0.12**
										% Expanded Uncertainty $U(y)$% (k=2)		**0.12**

4. Conclusions

A potentiometric titrimetry method for the determination of potassium iodate purity was established and developed at TUBITAK UME. Although this method is suitable for routine analysis, it can also be used in purity determinations in certified material production. The most important feature of this study is that it includes the most detailed uncertainty budget evaluation conducted in these analyses.

The acceptable expanded uncertainty value for the purity determination of potassium iodate was achieved in which the expanded uncertainty value had been targeted below the level of 0.5%.

Ethics in Publishing

There are no ethical issues regarding the publication of this study.

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