HIRANUMA APPLICATION DATA	Automatic Titrator	Data No.	O3	Feb. 03, 2022
Factor standardization	**Standardization of sodium thiosulfate titrant**			

1. Abstract

Sodium thiosulfate standard solution is used as a titrant for iodometric titration method. In iodometric titration, an equivalent amount of iodine (I_2) is produced by reacting the oxidant component in measurement sample with the added potassium iodide (KI). The generated iodine (I_2) is titrated with sodium thiosulfate standard solution, which enables the titration of the oxidant component indirectly.

Factors are indicated on the commercially available standard solution for volumetric analysis. The factor determination is required when the standard solutions are prepared in the laboratory. Also it is effective to check the repeatability by the factor measurement using a standard material to check the performance of titrator system. *Japanese Industrial Standard* JIS K 8001 and the *Japanese Pharmacopoeia* describe that potassium iodate (KIO_3), which is a standard material for a volumetric analysis, should be used for the factor determination of sodium thiosulfate standard solution.

The measurement procedure is as follows. The potassium iodate (KIO_3) standard solution is taken into an Erlenmeyer flask with a stopper by volumetric pipet, add sulfuric acid to acidify the solution, and then add potassium iodide (KI) to it. Promptly the stopper is attached on the flask and left to stand for 10 minutes, equivalent amounts of iodine (I_2) to potassium iodate (KIO_3) are produced according to equation (1). The factor is determined by performing potentiometric titration of this iodine (I_2) with sodium thiosulfate standard solution according to equation (2). 6 mol of sodium thiosulfate indirectly reacts quantitatively with 1 mol of potassium iodate (KIO_3), and the titration curve shows an inflection point at the end point.

$$KIO_3 + 5KI + 3H_2SO_4 \rightarrow 3I_2 + 3K_2SO_4 + 3H_2O \quad \cdots(1)$$

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI \quad \cdots(2)$$

1) Japanese Pharmacopoeia Eighteenth Edition
2) Japanese Industrial Standard JIS K8001 General rules for test methods of reagents

2. Configuration of instruments and reagents

(1) Configuration of instruments

Main unit	: Automatic Titrator	COM Series
Electrodes	: Platinum-reference combination electrode (long type)	PR-733BZ
Stirrer	: In order to attach a long-type electrode compatible with the Erlenmeyer flask, it is necessary to add or change some parts of the stirrer, as explained in section 5. (3).	

(2) Reagents

Titrant : 0.1 mol/L (0.1 N)*1 sodium thiosulfate standard solution (Buret No. 1)

Standard material : 1/60 mol/L (0.1 N)*1 Potassium iodate (KIO_3) standard solution (f = 1.003)
Prepared by dissolving standard material for volumetric analysis
(Certified value of purity for the standard material in this report: 99.97 %)

Additive reagent : Diluted sulfuric acid solution (Approx. 16 %)
Prepared by slowly adding 10 mL of sulfuric acid to 90 mL of DI water.
Potassium iodide (KI)

*1: Regarding the normality (N) of the concentration unit, it is explained in section 5. (2).

3. Measurement procedure

(1) Take 10 mL of 1/60 mol/L potassium iodate (KIO_3) standard solution into a 200 mL Erlenmeyer flask with volumetric pipet.

(2) Add 25 mL of DI water, 10 mL of diluted sulfuric acid solution and a stirrer bar to the flask. Swirl the flask gently.

(3) Add 2 g of potassium iodide (KI) into the flask and promptly attach a stopper on the flask. Swirl the flask gently.

(4) Leave to stand for 10 minutes.

(5) Add 100 mL of DI water to the flask.

(6) Immerse the electrode and start the measurement. Titration is performed with 0.1 mol/L sodium thiosulfate standard solution, and the inflection point on the titration curve is detected as the end point.

(7) Perform the blank test with the same procedure of sample measurement.

4. Measurement conditions and results

Examples of titration conditions

Blank measurement

Cndt No.	1							
Method	Auto		ConstantNo.	1		Mode No.	18	*2
Buret No.	1		Size	0	g	Pre Int	0	sec
Amp No.	1		Blank	0	mL	Del K	0	
D. Unit	mV		Molarity	0.1	N	Del Sens	0	mV
S-Timer	5	sec	Factor	0		Int Time	3	sec
C.P. mL	0	mL	K	0		Int Sens	3	mV
T Timer	0	sec	L	0		Brt Speed	2	
D.P. mL	0	mL				Pulse	40	
End Sens	300		Unit	mL				
Over mL	0.5	mL	Formula	D				
Max.Vol.	1	mL	Digits	3				

*2: Since the maximum change in electrode potential is shown at the first or the second drop of this blank titration, no clear inflection point appears on the titration curve. To detect this maximum change as an end point, set Mode No. to which the blank mode function is assigned, Mode No.12-19 for COM-A19.

Factor standardization measurement with potassium iodate (KIO_3)

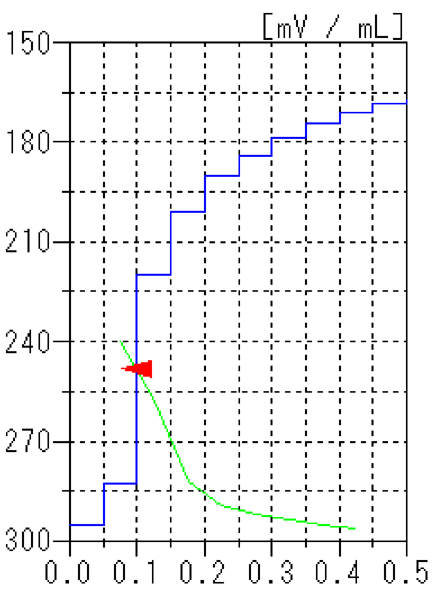
Cndt No.	2							
Method	Auto		ConstantNo.	2		Mode No.	5	
Buret No.	1		Size	10	mL	Pre Int	0	sec
Amp No.	1		Blank	0.076	mL	Del K	5	
D. Unit	mV		Molarity	0.1	N	Del Sens	0	mV
S-Timer	5	sec	Factor	1.003	*3	Int Time	3	sec
C.P. mL	0	mL	K	0		Int Sens	3	mV
T Timer	0	sec	L	0		Brt Speed	2	
D.P. mL	1.0	mL				Pulse	40	
End Sens	300		Unit	Fact1				
Over mL	0.5	mL	Formula	S/(D-B)*F				
Max.Vol.	20	mL	Digits	4				

*3: Factor of 1/60 mol/L potassium iodate (KIO_3) standard solution

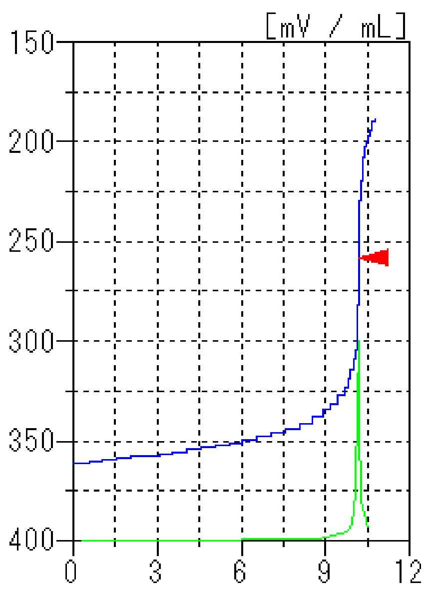
Measurement results

Measurement results of factor standardization

Sample	Measurement No.	Sample size (mL)	Titrant volume (mL)	Factor	Statistical results		
Blank	1	-	0.074	-	Avg.	0.076	mL
	2	-	0.078	-			
Potassium iodate standard solution	1	10	10.165	0.9942	Avg.	0.994	
	2		10.176	0.9931	SD	0.001	
	3		10.172	0.9935	RSD	0.06	%



Blank measurement



Factor standardization measurement

Examples of titration curves

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5. Note

(1) About a sampling of the standard material

Potassium iodate (KIO_3) is used for the standardization of sodium thiosulfate standard solution in redox titration. The standard material for volumetric analysis comes with a certificate value of the purity and uncertainty. If the certification and traceability are required for the management of test result, such as quality records, the standard material for volumetric analysis is used. It is necessary to prepare the standard material with pretreatment such as drying as described in its instruction before use.

In this report, the standard solution prepared from solid of potassium iodate (KIO_3), which is a standard material for volumetric analysis, is used as the standard sample. Otherwise, solid potassium iodate (KIO_3) can be directly used as the standard sample for this titration. However, in that case, the potassium iodate (KIO_3) should be weighed accurately in small amounts as about 50 mg or less estimated from the reaction ratio shown in the following formula (3).

1 mL of 0.1 mol/L sodium thiosulfate = 3.567 mg of potassium iodate (KIO_3) ・・・(3)

(2) Concentration of potassium iodate (KIO_3) standard solution to prepare

When a standard solution is used as the standard sample for factor standardization, the concentration of standard sample and titrant should be the same concentration in a normality (N) unit. The normality of concentration unit is indicated by the value obtained by multiplying the molar concentration by the valence of its chemical species. The valence in redox titration means how many mol of electrons are transferred by 1 mol of oxidant (or reductant). The normality (N) and valence of the reagents used in this report are as follows.

Sodium thiosulfate	: 0.1 mol/L = 0.1 N, (Valence: 1)
Potassium iodate (KIO_3)	: 1/60 mol/L = 0.1 N, (Valence: 6)

When a standard solution is used as the standard sample, the formula (Fact1) for calculating the factor of the titrant is indicated by [S / (D–B)×F]. This is derived from the following relational equation (4). The left side (subscript “s”) indicates the standard sample, and the right side (subscript “t”) indicates the titrant.

$$n_s \times M_s \times F_s \times S = n_t \times M_t \times F_t \times (D - B) \quad \cdots (4)$$

Standard solution		Titrant	
n_s	: Valence	n_t	: Valence
M_s	: Molarity	M_t	: Molarity
F_s	: Factor (Known)	F_t	: Factor (Unknown)
S	: Sample size (mL)	D-B	: Titrant volume at end point (mL)

If the standard sample and the titrant have the same normality (N), the product of valence and molarity on the right and left sides will be equal as [$n_s \times M_s = n_t \times M_t$], and this term can be omitted from equation (4). By converting equation (4) into a form that finds an unknown “F_t”, the equation [S / (D–B) × F] of “Fact1” is obtained. For this reason, when “Fact1” is selected for the calculation formula, it is necessary to prepare the standard sample and the titrant with the same concentration in normality (N).

(3) About electrodes and stirrers that fit in Erlenmeyer flasks

In this report, since a 200 mL Erlenmeyer flask is used as a titration vessel, platinum-reference combination electrode PR-733BZ (Long type) was used. The stirrer is modified to accommodate Erlenmeyer flasks as shown in Fig. 1 to attach the long type electrode. The figure below is a modification example of the Stirrer K-3000T attached to the titrator COM-A19.

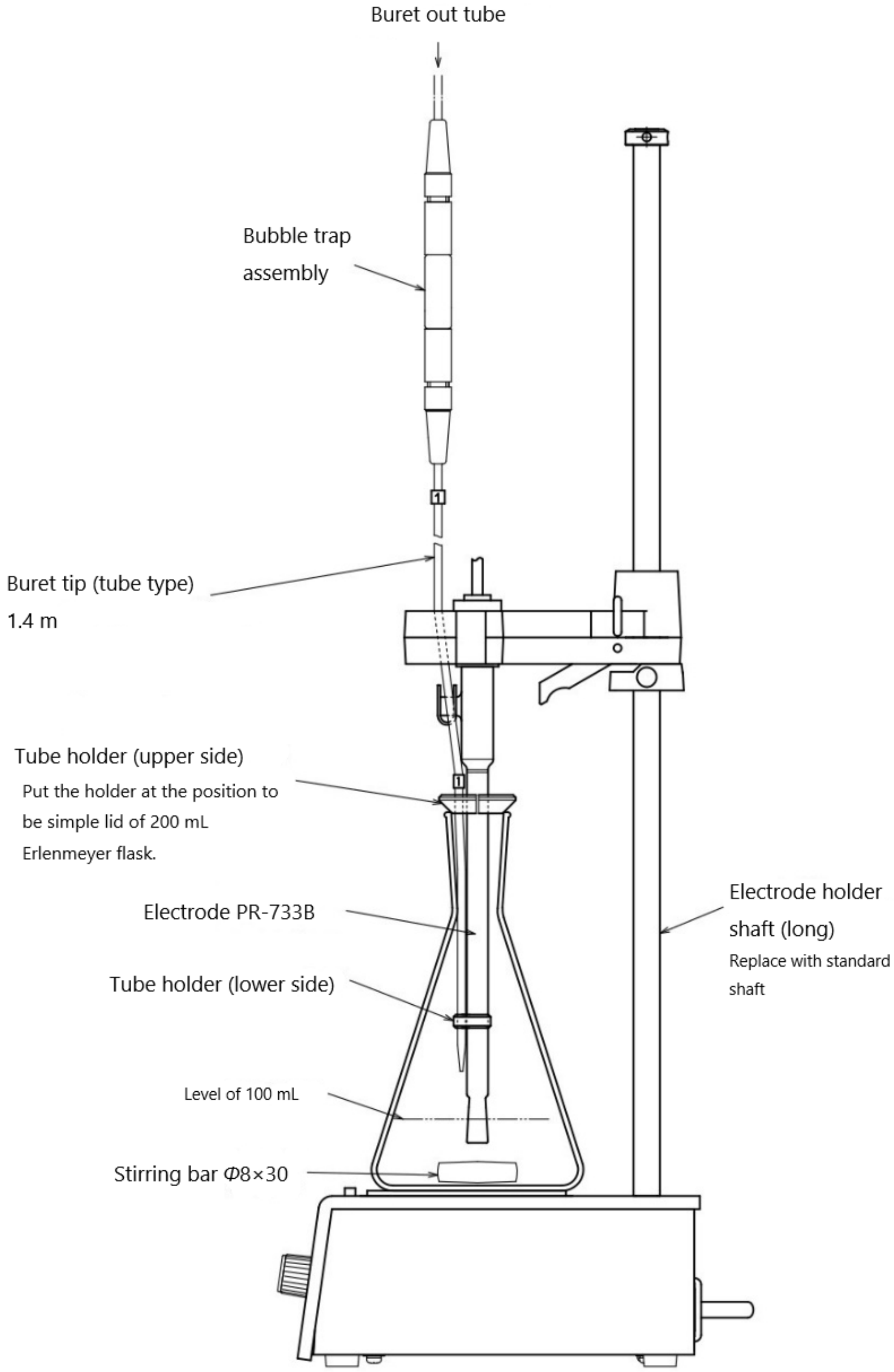

Figure 1 A set of electrode and stirrer parts for Erlenmeyer flasks

(4) How to check the performance of the titrator with sodium thiosulfate titrant without using an Erlenmeyer flask

In this report, an Erlenmeyer flask with a stopper is used as the titration vessel in order to titrate iodine (I_2) generated from equivalent amount of potassium iodate (KIO_3), which is a standard substance for volumetric analysis. For this reason, it is necessary to replace or add parts for the electrodes and stirrer as shown in section 5. (3).

If purpose of the measurement is not to determine the factor of sodium thiosulfate and just to check the performance of a titrator system (device, electrode, sodium thiosulfate standard solution), it is able to use iodine (I_2) standard solution as the standard sample. In that case, a beaker can be used as the titration vessel. The electrodes that can be used are not limited to the long and combination type, and can also be used with the half-cell type, such as PT-301 and RE-201Z.

However, since the iodine (I_2) standard solution is inferior in stability to potassium iodate (KIO_3), it is not recommended to use it for factor determination of sodium thiosulfate. Otherwise, it can be used for the performance check of the titrator system based on repeatability. Details are described in Application Data No. O7.

Keywords：Factor standardization, Redox titration, Sodium thiosulfate, Potassium iodate