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General rules for methods of
potentiometric, amperometric,
coulometric, and Karl-Fischer
titrations

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electro-analytical methods, instrumental methods of analysis

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General rules for methods of potentiometric, amperometric, coulometric, and Karl-Fischer titrations

1 Scope This Japanese Industrial Standard specifies general rules applicable when quantitative analysis is carried out according to potentiometric, amperometric, coulometric, or Karl-Fischer titration.

Remarks 1 The normative references to this Standard are as follows.

JIS K 0050 *General rules for chemical analysis*

JIS K 0126 *General rules for flow injection analysis*

JIS K 0211 *Technical terms for analytical chemistry (general part)*

JIS K 0213 *Technical terms for analytical chemistry (electrochemistry division)*

JIS K 8322 *Chloroform*

JIS K 8540 *Sodium (+)-tartrate dihydrate*

JIS K 8574 *Potassium hydroxide*

JIS K 8777 *Pyridine*

JIS K 8891 *Methanol*

JIS K 8895 *2-methoxyethanol*

JIS K 8920 *Iodine*

2 The International Standard corresponding to this Standard is as follows.

ISO 760-1978 *Determination of water—Karl Fischer method (General method)*

Informative reference: In ISO 760 in which Karl-Fischer titration has been specified, in order to detect the end point of titration, two methods are specified, one is method by visual titration, and the other is electrically detecting method, however, the latter is recommended because of its accuracy for measurement, therefore in this Standard the electrically detecting method only is specified.

2 Matters in common Matters in common shall follow JIS K 0050.

3 Definitions For the purpose of this Standard, main definitions are in accordance with JIS K 0211 and JIS K 0213, and for others the following definitions apply.

- (1) **titration curve** The curve expressing the state of progression of titration, for the purpose of deciding the end point of titration, in which any of indicator potential difference, pH, or indicator electric current (Y) is graduated on the ordinate axis, and either the volume of titrant needed for titration or the quantity of electricity (X) needed for generation of titration agent is graduated on the abscissa axis.

- (2) **differential titration curve** The curve plotted by graduating either difference quantity ($\Delta Y/\Delta X$) or differential quantity (dY/dX) of the titration curve on the ordinate axis and graduating the value of X on the abscissa axis.
- (3) **indicator electrode** An electrode for measuring either the electric potential or current that is used for determining the end point of titration.
- (4) **indicator potential difference** The electric potential difference of indicator electrode measured to the reference electrode.
- (5) **indicator current** The electric current flowing through indicator electrode.
- (6) **variation rate of potential difference** The value of $\Delta Y/\Delta X$ or dY/dX when the potential difference is denoted Y .
- (7) **solution to be titrated** A solution to be titrated for carrying out the determination of objective component.
- (8) **titrant** A solution containing the titration agent of known concentration.
- (9) **water reference solution** The solution in which the mass concentration of water is known.

4 Classification of analysis methods The analysis methods specified in this Standard shall be classified as follows.

- (1) **Potentiometric titration method** The titration method which uses indicator potential difference for detection of end point.
- (2) **Amperometric titration method** The titration method which uses indicator current for detection of end point.
- (3) **Coulometric titration method** The titration method in which titration agent is electrolytically generated and the amount of objective component is obtained from the quantity of electricity required for its generation.
- (4) **Karl-Fischer titration method** The titration method to obtain water content making use of Karl-Fischer reagent.

Remarks: Potentiometric titration method and amperometric titration method are both named based on the physical quantity employed for the end-point detection, therefore they may overlap with coulometric titration method.

5 Potentiometric titration method

5.1 Apparatus

5.1.1 Configuration The potentiometric titration apparatus is composed of, a titration part, control part, and display-recording part. Its example is shown in Fig. 1.

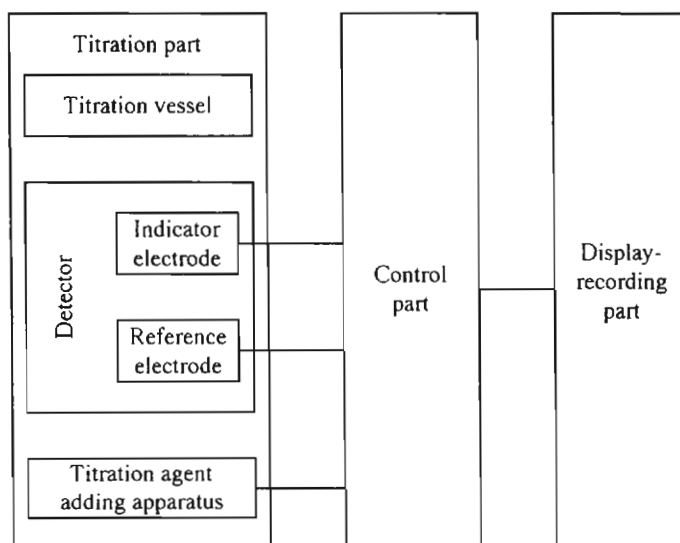


Fig. 1 Configuration of potentiometric titration apparatus (example)

5.1.2 Titration part Titration part is composed of, a titration vessel, detector, and titration agent adding apparatus.

- (1) **Titration vessel** The titration vessel is a vessel for titration, and is capable of being equipped with a detector and titration agent adding apparatus, and of agitating the solution. The material of the vessel shall be resistant against dissolving and deterioration.
- (2) **Detector** The detector is composed of an indicator electrode and reference electrode.
- (3) **Titration agent adding apparatus** The titration agent adding apparatus is an apparatus for quantitatively adding of titrant ⁽¹⁾ when titration solution is used, and it shall be as specified in 7.1.2 (3) when coulometric titration is used.

Note ⁽¹⁾ For instance, a buret or automatic buret.

5.1.3 Control part The control part shall have performances to amplify indicator electric potential difference by means of an amplifier with high input resistance, and to transduce it into the signal by which the display-recording part and titration agent adding apparatus are operated.

5.1.4 Display-recording part The display-recording part shall have performances to display or record the indicator electric potential difference. As occasion demands, the device to display or record titration curve, titration results, etc. is attached.

Remarks: A pH meter may be used in place of a control part and display-recording part.

5.2 Procedures

5.2.1 Preparation of titration curve or differential titration curve Prepare the titration curve or differential titration curve by plotting the indicator potential difference ⁽²⁾ or pH on Y axis and the volume of titrant on X axis. Carefully plot the curve to make the curve near its end point clear. In the case of coulometric titration, the quantity of electricity fed into

titration agent adding apparatus or the volume of titration agent calculated from it shall be plotted on X axis.

Note (2) The absolute value may be employed as Y , if any confusion is not anticipated.

5.2.2 Determination of end point The determination of end point shall be as follows:

- (1) When the titration curve is used, either of next two methods shall be used.
 - (a) **Inflection-point method** When the inflection point of or the maximum inclination point of the titration curve is found with necessary accuracy, take the reading on abscissa as the end point.
 - (b) **Intersecting-point method** As shown in Fig. 2, draw two lines, with 45° gradient, tangential to the titration curve, draw another line which is equidistant and parallel to these two lines, and read the intersecting point of the titration curve and this line on abscissa as the end point.
- (2) When employing differential titration curve, read the point where the absolute value of variation rate of potential difference shows the maximum value on the abscissa, to find the end point.

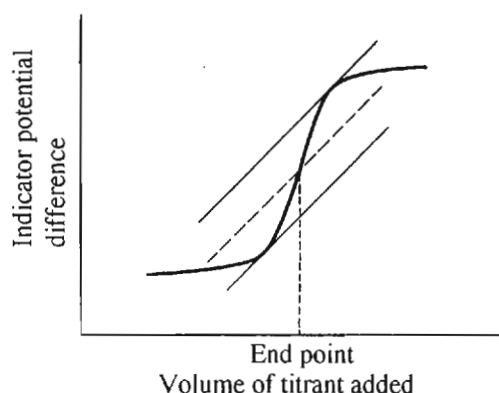


Fig. 2 Determination of end point (example)

5.2.3 Manual titration

- (1) The preparation of titration curve shall follow 5.2.1.
- (2) The determination of end point shall follow 5.2.2.
- (3) Other procedures than above shall comply with JIS K 0050 as appropriate.

5.2.4 Automatic titration Among automatic titration, there are the titration by automatic end-point detecting type, titration by end-point potential setting type, and titration by titration-curve automatic recording type.

- (1) **Titration by automatic end-point detecting type** Detect the point where the variation rate of potential difference becomes the maximum, make it the end point, and express or record any one of the volume of titrant, or the quantity of electricity supplied to the titration agent adding apparatus, or the results obtained by operational treatment of them.

- (2) **Titration by end-point potential setting type** Make the instant when indicator potential difference has reached the preliminarily set value as the end point, and express or record any one of the volume of titrant, or the quantity of electricity supplied to the titration agent adding apparatus, or the results obtained by operational treatment of them.
- (3) **Titration by titration-curve automatic recording type** Record the titration curve or differential titration curve. The way to determine the end point shall follow 5.2.2.

5.3 Arrangement of record When potentiometric titration is carried out, the items, which are thought to be necessary among the following items, shall be arranged and recorded. In the case of coulometric titration, however, it shall be as stated in 7.3.

- (1) Date and name of measurer
- (2) Manufacturer's name and type code of potentiometric titration apparatus. In the case where accessories are used, their names and types.
- (3) Preparation method of solution to be titrated
- (4) Composition and standardization method of titrant
- (5) Type and specification of indicator electrode and reference electrode
- (6) Titration conditions (temperature, condition for agitating, titration rate, existence of inert-gas ventilation, or others)
- (7) Volume of titrant required until end point, and indicator potential difference or pH value at end point (or the preliminarily set indicator potential difference or pH value in the case of automatic titration of end-point potential setting type)
- (8) Results of titration
- (9) Other matters

5.4 Maintenance and control

5.4.1 Installation of potentiometric titration apparatus The potentiometric titration apparatus shall be installed at a place complying with the following requirements:

- (1) The atmosphere shall be at a temperature 5 °C to 35 °C, a relative humidity not exceeding 85 % and shall not fluctuate rapidly.
- (2) There shall be no vibration, nor water leakage, nor direct sunshine.
- (3) Corrosive gas and dust shall be little and the ventilation shall be good.
- (4) There shall be no electrical noise which may cause interference.

5.4.2 Precautions for safety

- (1) All electrical wirings shall be electrically safe, and their insulation and earthing shall be securely executed.
- (2) The sample and reagents shall be handled carefully by taking their explosiveness, inflammability, poisonousness and deleteriousness sufficiently into consideration. When discarding them, they shall be stabilized and made innocuous.

5.5 Matters to be described on detail specification At specifying the analysis method by potentiometric titration method, at least the following items shall be specified. However, in the case of coulometric titration method, the matters shall be as specified in 7.5.

- (1) Objective component at measuring and its concentration range
- (2) Sampling method and preservation method of sample
- (3) Preparation method of solution to be titrated
- (4) Components, concentration range, and standardization method of titrant
- (5) Type and specification of indicator electrode and reference electrode
- (6) Determination method for end point
- (7) Number of times of titration
- (8) Expression method of analysis results

Remarks: Flow injection titration method may be used. The detail of titration method is as stated in JIS K 0126.

6 Amperometric titration method

6.1 Apparatus

6.1.1 Configuration The amperometric titration apparatus is composed of, a titration part, control part, and display-recording part. Its example is shown in Fig. 3 and Fig. 4.

6.1.2 Titration part The titration part is composed of, a titration vessel, detector, and titration agent adding apparatus.

- (1) **Titration vessel** The titration vessel shall be as specified in 5.1.2 (1).
- (2) **Detector** When amperometric titration apparatus uses one indicator electrode, the detector is composed of an indicator electrode, reference electrode, and auxiliary electrode. When the reference electrode is also used as the auxiliary electrode, the surface area of the reference electrode shall be 100 times or more than that of the indicator electrode, and the internal resistance of detector shall be 500 Ω or less. When amperometric titration apparatus has two indicator electrodes, the detector shall be composed of a pair of indicator electrodes identical in material and shape.
- (3) **Titration agent adding apparatus** The titration agent adding apparatus shall be as specified in 5.1.2 (3).

6.1.3 Control part The control part is composed of, the part which has the performance to actuate the display-recording part, the titration agent addition apparatus, etc. by amplifying the indicator current and a potentiostat. The potentiostat controls the electric potential of indicator electrode to the reference electrode, or the potential difference between two indicator electrodes. In such a case that the reference electrode also serves as the auxiliary electrode, or two indicator electrodes are used, a constant-voltage d.c. power source can be used instead of the potentiostat.