

<i>Category</i>	<i>Potentiometric Titrator COM series</i>
<b>Resins/Rubber/Adhesives /Paints/Electronics etc...</b>	<b>Epoxy equivalent in epoxy resin</b> by Acid/base titration method (non-aqueous)
<b>Referenced methods</b>	<b>JIS K7236, ISO 3001</b>

*Key words;* epoxy resins, epoxy equivalent, adhesives,

**Outline**

Epoxy resins have excellent properties of chemical and heat resistance, electrical insulating property and adhesion, a wide range of applications, especially utilized as sealant for electronic elements on the IC.

Epoxy is the general term for a group of chemical compounds in which two or more epoxide groups ( $\begin{matrix} \text{CH}_2 & - & \text{CH} \\ & \diagdown & / \\ & \text{O} & \end{matrix}$ ) are bound in each monomer. Epoxy does not become harden in itself, thus it is necessary to add curing agent or catalyst to form hardener compounds. By adding the hardener such as fatty amine, the amine groups react with the epoxide groups to form a covalent bond, resulting a thermosetting resin. The amount of the hardening agent corresponds to the epoxy equivalent of each epoxy resin (mass of the resin containing one equivalent of epoxy group). Thus, the process of determining the epoxy equivalent is an important part of quality control.

**Reagents**

<i>Titrant</i>	: 0.1mol/L perchloric acid (in acetic acid)
<i>Titration solvent</i>	: Chloroform 10mL Acetic acid 20mL } per measurement
<i>Reaction agent</i>	: Tetraethylammonium bromide (in acetic acid) 100g tetraethylammonium bromide is dissolved with 400mL of acetic acid.

**Instruments & Electrodes**

Recommended automatic titrator	<b>COM-1700S / COM-1600S</b>
<ul style="list-style-type: none"> <li>• <b>GE-101B</b> Glass electrode</li> <li>• <b>RE-201</b> Reference electrode*</li> </ul>	} standard accessories
(*replace the electrolyte with saturated sodium perchlorate in acetic acid)	



**COM-1700S**  
(built-in printer)

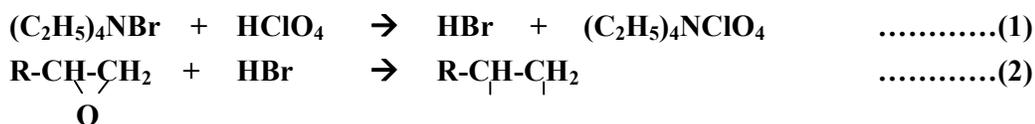


**COM-1600ST**  
(incl. optional thermal printer PR-2000T2)

**Summary of Test Method**

A weighed quantity of sample as recommended below is dissolved in 10mL of chloroform, add 20mL of acetic acid and 10mL of tetraethylammonium bromide in acetic acid. Titrate with 0.1mol/L perchloric acid in glacial acetic acid by potentiometric titration method based on the chemical reactions shown formula (1) and (2).

Estimated epoxy equivalent	Recommended size of test portion
180 ~ 190	0.1 ~ 0.16g
450 ~ 500	0.3 ~ 0.4g



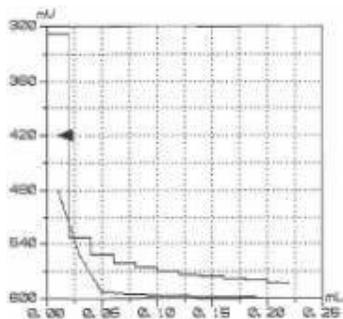
**Condition parameters (example)**

Master File 1 Condition 1 (for BLANK)				Master File 2 Condition 2 (for measurement)			
Method	Auto			Method	Auto		
Buret No.	1	Mode No.	19	Buret No.	1	Mode No.	23
Amp. No.	1	Pre Int	0 sec	Amp No.	1	Pre Int	0 sec
Meas Unit	mV	Del K	0	Meas Unit	mV	Del K	0
S-Timer	10 sec	Del Sens	0 mV	S-Timer	10 sec	Del Sens	0 mV
CP mL	0 mL	Int Time	5 sec	CP mL	0 mL	Int Time	5 sec
DP mL	0 mL	Int Sens	3 mV	DP mL	0.1 mL	Int Sens	5 mV
End Sens	500	BrT Speed	2	End Sens	300	BrT Speed	2
Over mL	0.1 mL	Pulse	16	Over mL	0.2 mL	Pulse	40
Max volume	20 mL			Max Volume	20 mL		
Unit	mL			Unit	E/E		
Size	0 g			Size	--- g		
Blank	0 mL			Blank	BLANK result value		
Factor	0			Factor	Titre of the titrant		
Molarity	0			Molarity	0.1 mol/L		
K	0			K	※Temperature correction factor value		
L	0			L	0		
Formula	D			Formula	1000*S/((D-B)*K*F*M		

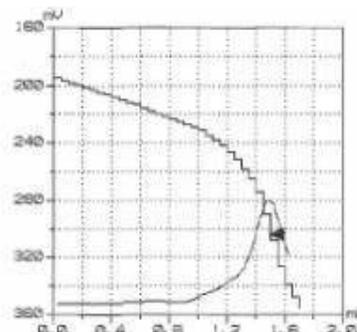
※Temperature correction factor= 1-(t-t<sub>s</sub>) / 1000

where: t: temperature of the titrant during the measurement  
t<sub>s</sub>: temperature of the titrant for standardization

**Titration curve examples**



-Blank-



-Sample measurement-

**Tips for Measurements**

1. Solvents

Choose an optimum solvent such as toluene, dioxane as well as chloroform, which can dissolve the sample well. Heat the sample if required long time to dissolve.

2. Maintenance of electrode

Since resin components may adhere to the electrodes after measurement, clean and rinse well with the titration solvent prior to be ready for the next measurement.

3. Effect of water on the titration curve

If water is mixed into the non-aqueous system, change in slope of the titration curve is very subtle and no clear end point is obtained.

4. Temperature of the titrant

Since the titration solvent used is acetic acid-base, the expansion coefficient is large. Thus, it is necessary to compensate with the factor value which is calculated from the temperature differences between the temperature of the titrant for the standardization and that for the measurement.

For more information, please feel free to contact:

**Hiranuma Sangyo Co., Ltd.**

1739 Motoyoshida-cho, Mito, Ibaraki 310-0836 JAPAN

Phone: +81-29-247-7343 / Fax: +81-29-247-0381

URL <http://www.hiranuma.com> E-mail [info@hiranuma.com](mailto:info@hiranuma.com)



ISO 9001  
ISO 13485 Certified



ISO 14001 Certified

ⓘ When using this homepage, we recommend Chrome browser. Chrome can translate web

pages.

ABOUT US

PRODUCT

APPLICATIONS

FAQ

CONTACT

<b>HIRANUMA APPLICATION DATA</b>		Automatic Titrator	Data No.	M1	Apr. 5, 2019
<b>Resins, Oils and Fats, Rubber, Adhesives, Paints</b>		<b>Epoxy equivalent determination of epoxy resins</b>			

## 1. Abstract

Epoxy resins have competent characteristics such as chemical resistance, heat resistance, and electrical properties. They are widely used for various materials like sealant of electronic device (IC).

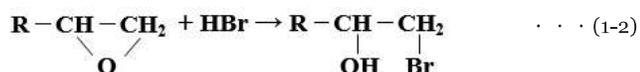
Epoxy resin is generic name of compounds which have two or more epoxy group in one molecule, it does not harden by itself. The addition of catalyst or hardener is required for curing. It becomes thermoset resin through addition polymerization with epoxy group by the hardener (fatty amine etc.). The additive amount of hardener corresponds to epoxy equivalent (mass of resin including one-equivalent epoxy group) of each epoxy resin. The determination of epoxy equivalent is quite important process for quality control. The measurement method of epoxy equivalent is defined in JIS (Japanese Industrial Standards) K7236:2001. Measurement is performed as follows:

- 1) Weigh the sample accurately and dissolve it in chloroform.
- 2) Add acetic acid and tetraethyl ammonium bromide – acetic acid solution.
- 3) Perform potentiometric titration with 0.1 mol/L perchloric acid – acetic acid standard solution.

Perchloric acid reacts with tetraethylammonium bromide and generates hydrogen bromide by addition of perchloric acid – acetic acid standard solution. (Refer to the reaction formula 1-1.)

The generated hydrogen bromide reacts with epoxy group. (Refer to the reaction formula 1-2.)

When all epoxy groups are reacted and hydrogen bromide gets excess, this point is detected as the endpoint to determine epoxy equivalent.



## 2. Configuration of instruments and reagents

### (1) Configuration

Main unit : Hiranuma Automatic Titrator COM series

Electrode : Glass electrode GE-101B

Reference electrode RE-201Z

\*Inner solution has to be changed to saturated sodium perchlorate in acetic acid.

### (2) Reagents

Titrant : 0.1 mol/L Perchloric acid – acetic acid standard solution

Solvent : 10 mL of chloroform (can be increased up to 30 mL when sample is macromolecule.)

20 mL of acetic acid

Additive : Tetraethylammonium bromide in acetic acid solution

100 g of tetraethylammonium bromide is dissolved in 400 mL of acetic acid.

## 3. Measurement procedure