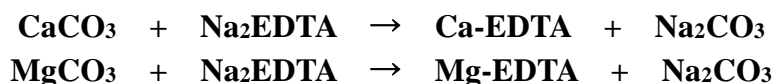| *HIRANUMA APPLICATION DATA*	Automatic Titrator	Data No.	D2	Nov. 14, 2018
Environment	**Total hardness in tap water**			

1. Abstract

Hardness in water is total amount of calcium and magnesium ion in water converted to mg/L of comparable calcium carbonate. "Hardness" has the following types:

(1) Total hardness   Total amount of calcium and magnesium ions

(2) Calcium hardness   Calcium ion

(3) Magnesium hardness   (Total hardness) – (Calcium hardness)

(4) Non-carbonate hardness (Permanent hardness)

(5) Carbonate hardness (Temporary hardness)

These are stipulated in some applicable standard such as *Standard Methods for the Examination of Water*, *Standard Methods of Analysis for Hygienic Chemists*, and JIS K0101 *Testing methods for industrial water* etc.

This report introduces an example for determination of total hardness in tap water with photometric titration method using EDTA standard solution according to the *Standard Methods for the Examination of Water*.

Take 100 mL of sample and add 1 mL of 0.01 mol/L magnesium chloride, 2 mL ammonia buffer, and 0.2 mL of EBT indicator. Titrate with 0.01 mol/L EDTA standard solution (red →blue color). Perform the same procedure for 100 mL of DI water instead of sample as blank measurement.

$$CaCO_3 \; + \; Na_2EDTA \; \rightarrow \; Ca\text{-}EDTA \; + \; Na_2CO_3$$
$$MgCO_3 \; + \; Na_2EDTA \; \rightarrow \; Mg\text{-}EDTA \; + \; Na_2CO_3$$

2. Configuration of instruments and reagents

(1) Configuration of instruments

     Main unit   : Hiranuma Automatic Titrator   COM Series

         (M type photometric unit for photometric titration with 650 nm optical filter)

(2) Reagents

     Titrant   : 0.01 mol/L EDTA standard solution

     Additive solution   : 0.01 ml/L Magnesium chloride solution

     Buffer solution   : Ammonium chloride-ammonia buffer solution (pH 10)

         Dissolve 6.75 g of ammonium chloride in 30 mL of DI water, add 57 mL of ammonia solution, and dilute to 100 mL with DI water.

     Indicator   : EBT Indicator

         Dissolve 0.5 g of eriochrome black T and 4.5 g of hydroxylammonium chloride in 100 mL of ethanol (95 % [v/v]).

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3. Measurement procedure

(1) Dispense 100 mL of sample into a 200 mL beaker with volumetric pipette.

(2) Add 1 mL of 0.01 mol/L magnesium chloride solution with volumetric pipette.

(3) Add 2 mL of ammonia buffer.

(4) Add 0.2 mL of EBT indicator.

(5) Immerse photometric probe and start titration with 0.01 mol/L EDTA standard solution.

(6) Perform the same procedure for 100 mL of DI water as blank measurement
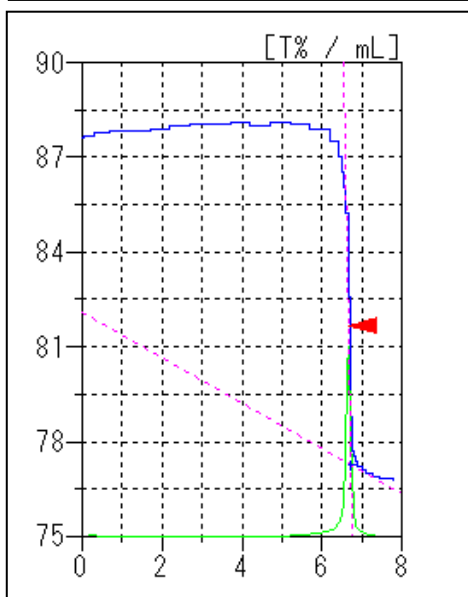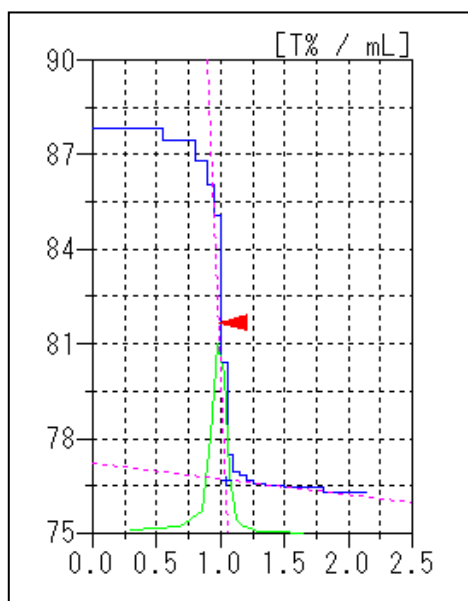
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4. Measurement conditions and results

Example of titration condition

Measurement of blank

Cndt No.	1							
Method	B cross	ConstantNo.		1		Mode No.	8	
Buret No.	1	Size		0	mL	Pre Int	0	sec
Amp No.	2	Blank		0	mL	Del K	5	
D. Unit	T%	Molarity		0.01	mol/L	Del Sens	0	mV
S-Timer	10	sec	Factor	1.001		Int Time	5	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	500		Unit	mL				
Over mL	1	mL	Formula	D				
Max.Vol.	20	mL	Digits	4				
			Auto In Pram.	Non				

Measurement of sample

Cndt No.	2							
Method	B cross	ConstantNo.		2		Mode No.	8	
Buret No.	1	Size		100	mL	Pre Int	0	sec
Amp No.	2	Blank		1.040	mL	Del K	5	
D. Unit	T%	Molarity		0.01	mol/L	Del Sens	0	mV
S-Timer	10	sec	Factor	1.001		Int Time	5	sec
C.P. mL	0	mL	K	100		Int Sens	3	mV
T Timer	0	sec	L	0		Brt Speed	2	
D.P. mL	0	mL				Pulse	40	
End Sens	500		Unit	PPM				
Over mL	1	mL	Formula	(D-B)*K*F*M*1000/S				
Max.Vol.	20	mL	Digits	4				
			Auto In Pram.	Non				

Measurement results

Measurement of blank

Number of Measurement	Size (mL)	Titrant Volume (mL)
1		1.041
2	-	1.041
3		1.038
Statistic calculation	Avg.	1.040 mL
	SD	0.0017 mL
	RSD	0.17 %

Measurement of sample

Number of Measurement	Size (mL)	Titrant Volume (mL)	Total hardness (ppm)
1	100	6.718	56.837
2	100	6.745	57.107
3	100	6.719	56.847
Statistic calculation	Avg.		56.9 ppm
	SD		0.153 ppm
	RSD		0.27 %

Examples of titration curves

5. Note

(1) Measurement

The total hardness in tap water can accurately be determined by photometric titration method with EBT indicator using photometric probe.

(2) End point detection

"Method" on the condition parameter is set to "B cross" because the point where indicator color change is completed is detected as endpoint. When the concentration of total hardness is relatively high and much titrant volume is required, "C.P. mL" function is useful. Titrant can be added at once by setting "C.P. mL" to a few mL smaller than titrant volume at the endpoint, it can reduce measurement time.

Keywords: Tap water, Total hardness, Photometric titration, EDTA standard solution

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