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EZ5002 Total Hardness & Calcium Hardness Analyser

Method and reagent sheets

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1. Legal information

Manufacturer: AppliTek NV/SA

Distributor: Hach Lange GmbH

The translation of the manual is approved by the manufacturer.

2. Analytical specifications

Please refer also to the respective technical datasheet at Hach Support Online.

Total Hardness & Calcium Hardness - All specifications			
Analysis method	Colorimetric titration by EDTA using colour indicators calmagite (TH) and hydroxynaphthol blue at 610 nm (CaH)		
Parameter	Total hardness (TH); Calcium hardness (CaH) - CaCO_3		
Cycle time	20 – 30 minutes (dilution + 10 min.)		
Limit of detection (LOD)	≤ 10 mg/L		
Precision/Repeatability	Better than 2% full scale range for standard test solutions		
Cleaning	Automatic; frequency freely programmable		
Calibration	Automatic, one-point calibration		
Validation	Automatic; frequency freely programmable		
Interferences	Some metal ions interfere by causing fading or indistinct end points or by stoichiometric consumption of EDTA. Suspended or colloidal organic matter also may interfere with the end point. Large amounts of colour and turbidity interferes. Fats, oil, proteins, surfactants and tar.		
Measuring ranges	% of range - Dilution		Low range (mg/L)
	A	10% of standard range	10
	B	25% of standard range	25
	C	50% of standard range	50
	0	standard range	100
	V	Internal dispenser dilution factor 5	500
	W	Internal dispenser dilution factor 10	1000
	X	Internal dispenser dilution factor 25	2500
	Y	Internal dispenser dilution factor 50	5000
			50000

3. Analysis method

Summary

The determination of Total Hardness and Calcium Hardness is based on two methods, combined in one analyser.

The Total Hardness concentration is determined in the 'TH' method. The Calcium hardness concentration is determined in the 'CaH' method. The concentration of all parameters is determined alternately in the 'Main'-method.

The calibration for Total Hardness is determined in the 'TH' method. The calibration for Calcium hardness is determined in the 'CaH' method.

Remark

The methods cannot be started at the same time.

3.1 Total Hardness

Summary

The determination of the total hardness concentration in water is based on the reaction of free calcium and magnesium with calmagite in an alkaline solution to form a purplish-red colour. The calcium/magnesium – indicator complex is released by titration with EDTA, causing a blue colour. The change from red to blue colour is a measurement for the amount of calcium and magnesium present in the sample. The colour change is measured at 620 nm

Analysis steps

The analysis vessel is cleaned and filled with fresh sample. After sampling, the acid solution, buffer solution and colour solution are added. The colorimetric titration with EDTA at 620 nm is performed. After the determination of the end point, the calcium and magnesium concentrations in the sample are determined.

Calibration

The calibration procedure measures a REF2 CaCO_3 solution (channel 10, REF2 valve) to adapt the slope factor by means of a one-point calibration.

3.2 Calcium Hardness

Summary

The determination of the calcium concentration in water is based on the reaction of free calcium and magnesium with Hydroxynaphthol blue in a strong alkaline medium (to mask the magnesium) to form a purplish-red colour. The calcium-indicator complex is released by titration with EDTA, causing a blue colour. The change from red to blue colour is a measurement for the amount of calcium present in the sample. The colour change is measured at 620 nm

Analysis steps

The analysis vessel is cleaned and filled with fresh sample. After sampling, the acid solution, buffer solution and colour solution are added. The colorimetric titration with EDTA at 620 nm is performed. After the determination of the end point, the calcium concentration in the sample is determined.

Calibration

The calibration procedure measures a REF2 CaCO_3 solution (channel 10, REF2 valve) to adapt the slope factor by means of a one-point calibration.

4. Reagents

⚠ CAUTION	
	Chemical exposure hazard. Obey laboratory safety procedures and wear all of the personal protective equipment appropriate to the chemicals that are handled. Read the safety data sheet from the supplier before bottles are filled or reagents are prepared. For laboratory use only. Make the hazard information known in accordance with the local regulations of the user.

⚠ CAUTION	
	Chemical exposure hazard. Dispose of chemicals and wastes in accordance with local, regional and national regulations.

4.1 Reagent overview and consumption

In the table below, the products that are needed to prepare the reagents are listed. The product name, the formula, the molecular weight, the CAS No. and the amount needed to prepare 1 litre of the reagents is given. Check the consumption of the reagents (28 days) to adapt the volumes needed.

Total HardnessProduct	Consumption	Consumption/28 days At rate 1 analysis/25 min	Recommended containers
Acid solution (TH)	~ 0.5 mL	< 1.7 L	Plastic – 2.5L
Acid solution (CaH)	~ 0.5 mL		
Buffer CaMg solution	~ 0.5 mL	< 1.0 L	Plastic – 2.5L
Colour CaMg solution	~ 0.5 mL	< 1.0 L	Plastic – 2.5L
Buffer Ca solution	~ 1.0 mL	< 1.0 L	Plastic – 2.5L
Colour Ca solution	~ 0.5 mL	< 1.0 L	Plastic – 2.5L
EDTA solution (TH)	Depending on concentration	1L < Volume < 24 L	Plastic – 10L
EDTA solution (CaH)	Depending on concentration		
REF2 Solution (TH+CaH)	~ 1 L / calibration	/	Plastic – 2.5 L

4.2 Storage and quality of chemicals

Quality of chemicals

All chemicals should be of ACS grade or better. We recommend the use of pro analysis chemicals.

Quality of water

Reagent grade, carbon dioxide-free de-ionized water must be used to prepare the chemical solutions and for rinse purposes.

Storage of Reagents

While operating the instrument, keep in mind the ambient temperature conditions as stated in the data sheet of the instrument.

Store the reagents cold; Store the reagents in the dark; Refresh the reagents after one month (unless stated differently in the chapters below).

4.3 Acid solution (0.5 M)

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
Hydrochloric Acid (36%)	HCl	36.46	7647-01-0	41.5 mL

Preparation:

Prepare a 0.5 M hydrochloric acid (HCl) solution. Dilute 41.5 mL of hydrochloric acid (HCl) in 500 mL de-ionized water and fill up to 1 litre with demineralized water.

4.4 Buffer CaMg solution

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
Ammonium chloride	NH ₄ Cl	53.49	12125-02-9	54 g
Ammonia solution 25%	NH ₄ OH	35.05	1336-21-6	350 mL
Mg-EDTA*	C ₁₀ H ₁₂ MgN ₂ Na ₂ O ₈ * 4H ₂ O	430.56	29932-54-5	5 g

*ethylenediaminetetraacetic acid magnesium disodium salt tetrahydrate

Preparation:

Dissolve 54 g of ammonium chloride (NH₄Cl) in de-ionized water using a volumetric flask of 1000 mL. Add 350 mL of ammonium hydroxide solution (NH₄OH 25%). Add 5 g Mg-EDTA, dissolve completely and fill up to 1 litre with de-ionized water.

Proposal for an alternative product:

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
**EDTA-K ₂ Mg * 2H ₂ O	C ₁₀ H ₁₂ K ₂ MgN ₂ O ₈ * 2H ₂ O	426.75	CAS 15708-48-2	4.96 g
***EDTA-Na ₂ Mg * xH ₂ O	C ₁₀ H ₁₂ N ₂ O ₈ .Mg.2Na	358.8	CAS 14402-88-1	4.17

**ethylenediaminetetraacetic acid dipotassium magnesium salt dihydrate

*** ethylenediaminetetraacetic acid magnesium disodium hydrate

4.5 Colour CaMg solution

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
Calmagite	HOC ₁₀ H ₅ [N=NC ₆ H ₃ (OH)CH ₃]SO ₃ H	358.37	3147-14-6	0.2 g

Preparation:

Dissolve approximately 0.2 g calmagite (HOC₁₀H₅[N=NC₆H₃(OH)CH₃]SO₃H) in 400 mL degassed de-ionized water using a volumetric flask of 1L. Fill up to the grade mark with de-ionized water.

4.6 Buffer Ca solution

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
Sodium hydroxide	NaOH	40.00	1310-73-2	20 g

Preparation:

Dissolve 20 g of sodium hydroxide (NaOH) in 500 mL de-ionized water using a volumetric flask of 1 litre. Dissolve completely and fill up to the grade mark with de-ionized water.

4.7 Colour Ca solution

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
Hydroxynaphtol blue (HNB)	C ₂₀ H ₁₁ N ₂ Na ₃ O ₁₁ S ₃	620.47	63451-35-4	0.4 g

Preparation:

Dissolve approximately 0.4 g hydroxynaphtol blue (HNB) in 500 mL de-ionized water using a volumetric flask of 1 litre. Fill up to the grade mark with de-ionized water.

4.8 EDTA solution

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
EDTA*	$C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$	372.2	6381-92-6	x g

*ethylenediaminetetraacetic acid disodium salt dihydrate

Preparation

Prepare a x M EDTA solution. Dissolve accurately x g ethylenediaminetetraacetic acid disodium salt dihydrate ($C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$) in 500 mL degassed de-ionized water and fill up to 1000 mL.

	Measuring range	Concentration EDTA solution	Amount to add to 1 litre
A	100 mg/L $CaCO_3$	0.005 M	1.861 g
B	250 mg/L $CaCO_3$	0.005 M	1.861 g
C	500 mg/L $CaCO_3$	0.01 M	3.722 g
0	1000 mg/L $CaCO_3$	0.02 M	7.444 g
V	5000 mg/L $CaCO_3$	0.02 M	7.444 g
W	10000 mg/L $CaCO_3$	0.02 M	7.444 g
X	25000 mg/L $CaCO_3$	0.02 M	7.444 g
Y	50000 mg/L $CaCO_3$	0.02 M	7.444 g

4.9 Calibration solution

Products	Formula	MW (g/mol)	CAS No.	Range	1 litre solution
Calcium chloride dihydrate	$CaCl_2 \cdot 2H_2O$	147.02	10035-04-8	≤ 1000 mg/L $CaCO_3$	14.702 g
				> 1000 mg/L $CaCO_3$	147.02 g

Preparation:

Range ≤ 1000 mg/L $CaCO_3$:

10000 mg/L $CaCO_3$ stock solution

Dissolve accurately 14.702 g calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) in 600 mL de-ionized water, using a volumetric flask of 1000 mL. Add de-ionized water up to the mark grade.

CaCO₃ standard solution – REF2

Prepare a standard solution for calibration according to the following table: take accurately x mL of the 10000 mg/L CaCO₃ stock solution and transfer into a volumetric flask of 1000 mL. Add de-ionized water up to the mark grade.

	Measuring range	Concentration REF2 solution	Amount to add to 1 litre
A	100 mg/L CaCO ₃	100 mg/L CaCO ₃	10 mL
B	250 mg/L CaCO ₃	250 mg/L CaCO ₃	25 mL
C	500 mg/L CaCO ₃	500 mg/L CaCO ₃	50 mL
0	1000 mg/L CaCO ₃	1000 mg/L CaCO ₃	100 mL

Range > 1000 mg/L CaCO₃:

100000 mg/L CaCO₃ stock solution

Dissolve accurately 147.02 g calcium chloride dihydrate (CaCl₂ * 2H₂O) in 600 mL de-ionized water, using a volumetric flask of 1000 mL. Add de-ionized water up to the mark grade.

CaCO₃ standard solution – REF2

Prepare a standard solution for calibration according to the following table: take accurately x mL of the 100000 mg/L CaCO₃ stock solution and transfer into a volumetric flask of 1000 mL. Add de-ionized water up to the mark grade.

	Measuring range	Concentration REF2 solution	Amount to add to 1 litre
V	5000 mg/L CaCO ₃	5000 mg/L CaCO ₃	50 mL
W	10000 mg/L CaCO ₃	10000 mg/L CaCO ₃	100 mL
X	25000 mg/L CaCO ₃	25000 mg/L CaCO ₃	250 mL
Y	50000 mg/L CaCO ₃	50000 mg/L CaCO ₃	500 mL

4.10 Cleaning solution (facultative)

The cleaning procedure should prevent any build-up of chemicals in the analyser. To obtain an effective cleaning procedure we recommend testing the cleaning solution and the cleaning interval for each application. Perform the selected cleaning solution and interval for a trial period, check then the effectiveness of the procedure and change if necessary.