DOC312.53.94406

EZ1304 Total Hardness & Calcium Hardness Analyser

Method and reagent sheets

11/2021, Edition 1.01

Table of Contents

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.

Hardness - All specifications				
Analysis method	Colorimetric measurement using calmagite or hydroxynaphtol blue colour solution			
Parameter	Total Hardness (TH), Calcium Hardness (CaH)			
Cycle time	Standard measurement cycle time: 20 minutes Internal dilution: + 5 min. per parameter External dilution: + 5 – 10 min. per parameter			
Limit of detection (LOD)	TH: ≤ 0.025 mg/L CaH: ≤ 0.005 mg/L			
Precision/Repeatability	Better than 2% full scale range for standard test solutions			
Cleaning	Automatic; frequency freely programmable			
Calibration	Automatic, 2-point; frequency freely programmable			
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)**	**High range (mg/L)**
TH	B	25% of standard range	0.025	0.25
	C	50% of standard range	0.025	0.50
	0	**standard range**	**0.05**	**1.0**
	W	internal dispenser dilution (factor 10)	0.5	10
	X	internal dispenser dilution (factor 25)	1.25	25
	Y	internal dispenser dilution (factor 50)	2.5	50
	Z	internal dispenser dilution (factor 75)	3.75	75
	5	internal dispenser dilution (factor 100)	5	100
	% of range - Dilution		**Low range (mg/L)**	**High range (mg/L)**
CaH	B	25% of standard range	0.005	0.25
	C	50% of standard range	0.005	0.50
	0	**standard range**	**0.025**	**1.0**
	W	internal dispenser dilution (factor 10)	0.25	10
	X	internal dispenser dilution (factor 25)	0.625	25
	Y	internal dispenser dilution (factor 50)	1.25	50
	Z	internal dispenser dilution (factor 75)	1.875	75
	5	internal dispenser dilution (factor 100)	2.5	100

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

Calcium or magnesium reacts with calmagite in a alkaline medium to form a red coloured complex. EDTA is added and binds with calcium and magnesium and the colour changes back to blue. The absorption change is measured at a wavelength of 610 nm.

Analysis steps

The analysis vessel is cleaned and filled with fresh sample. After sampling and addition of the acid, buffer and colour solution the initial absorbance value is measured at 610 nm. Next, the EDTA solution is added and after respecting a stirring period – performed to obtain complete colour development – the final absorbance value is determined. With the obtained absorbance values, the total hardness concentration can be calculated according to Beer’s law.

Calibration

The calibration procedure measures a REF1 $CaCO_3$ solution (channel 9, REF1 valve) and a REF2 $CaCO_3$ solution (channel 10, REF2 valve) to adapt the slope and offset factors by means of a two point calibration.

3.2 Calcium Hardness

Summary

The determination of the calcium hardness concentration in water is based on the reaction of free calcium with hydroxynaphthol blue in an alkaline solution to form a purplish-red colour. The calcium– indicator complex is release by adding EDTA, causing a blue colour. The change from red to blue colour is a measure for the amount of calcium present in the sample. The colour change is measured at 610 nm.

Analysis steps

The analysis vessel is cleaned and filled with fresh sample. After sampling and addition of the acid, buffer and colour solution the initial absorbance value is measured at 610 nm. Next, the EDTA solution is added and after respecting a stirring period – performed to obtain complete colour development – the final absorbance value is determined. With the obtained absorbance values, the calcium hardness concentration can be calculated according to Beer's law.

Calibration

The calibration procedure measures a REF1 $CaCO_3$ solution (channel 9, REF1 valve) and a REF2 $CaCO_3$ solution (channel 10, REF2 valve) to adapt the slope and offset factors by means of a two 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 tables 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 liter of the reagents is given. Check the consumption of the reagents (28 days) to adapt the volumes needed.

Product	Consumption	Consumption/28 days A rata 1 analysis/20 min	Recommended containers
Acid solution (TH)	~ 0.5 mL / analysis	~ 2.0 L	Plastic – 2.5 L
Acid solution (CaH)	~ 0.5 mL / analysis		
Buffer CaMg solution (TH)	~ 0.5 mL / analysis	~ 1.0 L	Plastic – 2.5 L
Buffer Ca solution (CaH)	~ 1 mL / analysis	~ 2.0 L	Plastic – 2.5 L
Colour CaMg solution (TH)	~ 0.5 mL / analysis	~ 1.0 L	Plastic – 2.5 L
Colour Ca solution (CaH)	~ 0.5 mL / analysis	~ 1.0 L	Plastic – 2.5 L
EDTA solution (TH)	~ 0.5 mL / analysis	~ 2.0 L	Plastic – 2.5 L
EDTA solution (CaH)	~ 0.5 mL / analysis		
REF1 solution (TH & CaH)	~ 1 L / calibration	/	Plastic – 1 L
REF2 solution (TH & CaH)	~ 1 L / calibration	/	Plastic – 1 L

4.2 DI-water overview and consumption

	Rinse water (mL/analysis) Type I		Dilution water (mL/analysis) Type I		Total (mL/analysis)	Consumption/28 days A rata 1 analysis/20 min
	TH	**CaH**	**TH**	**CaH**	**TH + CaH**	**TH + CaH**
B	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
C	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
0	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
W	60 mL	60 mL	15 mL	15 mL	150 mL	302 L
X	60 mL	60 mL	15 mL	15 mL	150 mL	302 L
Y	60 mL	60 mL	15 mL	15 mL	150 mL	302 L
Z	60 mL	60 mL	15 mL	15 mL	150 mL	302 L
5	60 mL	60 mL	15 mL	15 mL	150 mL	302 L

Remark

The indicated volumes are an estimation of the consumption for rinse and dilution water, based on a standard operating procedure, as defined in the specifications of the EZ analyser. Please be aware that, depending on the sample matrix, the rinse water volumes might increase.

4.3 Storage and quality of chemicals

Quality of chemicals

All chemicals should be of Reagent grade, ACS grade or better (*). The use of pro analysis chemicals is recommended. Poor quality of the reagents can affect the analyser performance.

(*) Analytical Reagent (AR), Guaranteed Reagent (GR), UNIVAR, AnalaR, Premium Reagent (PR), ReagentCertified ACS reagent, ACS Plus reagent, puriss p.a. ACS reagent, ReagentPlus®, TraceCERT®, Suprapur®, Ultrapur®, or better are also possible.

Quality of DI-water

All EZ analysers are tested with standard solutions, reagents and dilution water prepared using type I water or better as defined by ASTM D1193-91.

To achieve the specifications as stated on the data sheet, method and reagents sheet and acceptance test reports, the same water quality (or better) must be used for the preparation of the standard solutions, reagents and dilution water.

Additionally the water used for the preparation of the standard solutions for an EZ analyser must be free of the parameter or any of the interferences for the method of that EZ analyser.

Storage of Reagents

While operating the instrument, keep in mind the reagent requirements as stated in the reagent overview, the chapters below and/or in the data sheet of the instrument.

⚠ CAUTION	
⚠	For longer-term storage: Store the reagents cold; Store the reagents in the dark; If applicable: Store the reagents in a fridge during operation

⚠ CAUTION	
⚠	Refresh the reagents after one month (unless stated differently in the chapters below). Do not mix old reagents with freshly prepared reagents. Remove old reagents from the container before adding freshly prepared reagents.

Materials

In order to avoid Ca contamination in the reagents we recommend to prepare the reagents into dedicated plastic flasks. Prior to the use of the flask we recommend to rinse the flasks with acid (0,1M HCl) and pure water to clean any contamination.

4.4 Acid solution

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 36%) in 500 mL de-ionized water using a volumetric flask of 1000 mL. Mix and fill up to the grade mark with de-ionized water.

4.5 Buffer solution

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
Ammonium chloride	NH_4Cl	53.49	12125-02-9	54 g
Ammonia solution 25%	NH_4OH	35.05	1336-21-6	350 ml
Mg-EDTA*	$C_{10}H_{12}MgN_2Na_2O_8 * 4H_2O$	430.56	29932-54-5	5 g

*ethylenediaminetetraacetic acid magnesium disodium salt tetrahydrate

Preparation

Dissolve 54 g of ammonium chloride (NH_4Cl) in 500 mL de-ionized water using a volumetric flask of 1000 mL. Add 350 mL ammonia solution (NH_4OH 25%) and 5 g of Mg-EDTA ($C_{10}H_{12}MgN_2Na_2O_8 * 4H_2O$). Dissolve completely and 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 1000 mL. Dissolve completely and fill up to the grade mark with de-ionized water**.**

4.7 Colour CaMg solution

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
Calmagite	$HOC_{10}H_5[N=NC_6H_3(OH)CH_3]SO_3H)$	358.37	3147-14-6	0.2 g

Preparation

Dissolve 0.2 g of calmagite ($HOC_{10}H_5[N=NC_6H_3(OH)CH_3]SO_3H$)) in 500 mL de-ionized water. Mix and fill up to 1 litre with de-ionized water.

Stir the colour solution for 24h prior to use.

4.8 Colour Ca solution

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
Hydroxynaphthol blue (HNB)	$C_{20}H_{11}N_2Na_3O_{11}S_3$	620.47	63451-35-4	0.4 g

Preparation*:*

Dissolve approximately 0.4 g hydroxynaphthol blue (HNB) in 400 mL degassed de-ionized water using a volumetric flask of 1000 mL. Fill up to the grade mark with de-ionized water.

We recommend to use of HNB with following specifications:

Product	Brand	CAS No.	Product No.
Hydroxynaphthol blue (HNB)	Honeywell Fluka	63451-35-4	33936

4.9 EDTA solution (0.025M)

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
EDTA*	$C_{10}H_{14}N_2Na_2O_8 * 2H_2O$	372.2	6381-92-6	9.13 g

*ethylenediaminetetraacetic acid disodium salt dihydrate

Preparation

Dissolve 9.13 g of EDTA in 300 mL de-ionized water. Mix and fill up to 1 litre with de-ionized water.

4.10 Calibration solution

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
Calcium chloride dihydrate	$CaCl_2 * 2H_2O$	147.02	10035-04-8	1.4689 g

Preparation

1000 mg/L $CaCO_3$ stock solution

Prepare a stock solution of 1000 mg/L $CaCO_3$: Dissolve accurately 1.4689 g calcium chloride dihydrate ($CaCl_2 * 2H_2O$) in 300 mL de-ionized water using a volumetric flask of 1000 mL. Add de-ionized water up to the mark grade.

$CaCO_3$ standard solution – REF2

Prepare a standard solution for calibration according to the following table: take accurately x mL of the 1000 mg/L $CaCO_3$ stock solution and transfer into a volumetric flask of 1000 mL. Add de-ionized water up to the mark grade.

	Measuring range	Concentration REF2	Amount of stock solution to add to 1 litre
B	0.25 mg/L $CaCO_3$	0.25 mg/L $CaCO_3$	0.25 mL
C	0.50 mg/L $CaCO_3$	0.50 mg/L $CaCO_3$	0.50 mL
0	**1.0 mg/L $CaCO_3$**	**1.0 mg/L $CaCO_3$**	**1.0 mL**
W	10 mg/L $CaCO_3$	10 mg/L $CaCO_3$	10 mL
X	25 mg/L $CaCO_3$	25 mg/L $CaCO_3$	25 mL
Y	50 mg/L $CaCO_3$	50 mg/L $CaCO_3$	50 mL
Z	75 mg/L $CaCO_3$	75 mg/L $CaCO_3$	75 mL
5	100 mg/L $CaCO_3$	100 mg/L $CaCO_3$	100 mL

$CaCO_3$ standard solution – REF1

Prepare a standard solution of 0 mg/L $CaCO_3$. Use de-ionized water.

4.11 Cleaning solution (facultative)

The cleaning procedure should prevent any build-up of chemicals in the analyser. To obtain an effective cleaning procedure one has to test 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.

Change Information	
Date: 22/11/2021	Previous version: Edition 4 to Edition 1.01

Reason for Change

- Addition of extra ranges and obsolescence of the 10% range, the 4x dilution and 8x dilution in the in the portfolio of EZ1304
- Addition of water consumption
- Addition of information reagents

Description of Change

- Addition of estimated consumption of water for rinse and dilution (chapter 4.2)
- Addition of extra information regarding storage and quality of reagents (chapter 4.3)
- Addition of extra information regarding product quality for colour solution (chapter 4.8)
- Addition of extra ranges for internal dispenser dilution: 10x, 25x, 50x, 75x (chapter 4.10)