Determination of total hardness of water by complexonometric titration (EDTA)

SCOPE AND FIELD OF APPLICATION: The present method is used for the determination of total hardness of water in drinking water, ground water and surface water.

PRINCIPLE: The method is based on the reaction of heavy metal ions and alkaline earth metal ions (mostly Ca and Mg) with EDTA in basic solution. The sample is titrated with EDTA solution of known concentration until the initially obtained violet color of the solution has turned to stabile blue color. ET-00 serves as an indicator with this measurement.

The values of uncertainty components of volumetric ware are taken according to our experience, experiments carried out in our lab and data from manufactures of the volumetric ware. The users of these examples are advised to use this data only as the first approximation and substitute these uncertainty estimates by their own data that corresponds to the actual situation in their own lab.

Determination of the concentration of the EDTA standard solution

For the determination of the concentration of previously prepared EDTA solution (the titrant), the 0.05 M $MgSO_4$ standard substance solution was prepared by dissolving 0.05 mol $MgSO_4*7H_2O$ in a 1000 ml volumetric flask. 10 ml of $MgSO_4$ standard substance solution (V_{MgSO4}) was transferred to a 250 cm³ titration vessel and 50 cm³ of distilled water, 5 cm³ of ammonia buffer solution and a bit of indicator ET-00 were added. The standard substance solution was titrated until the initially obtained violet color of the solution had turned to stabile blue color. For the determination of the concentration of the EDTA standard solution (c_{EDTA}) 4 titrations were carried out.

Determination of total hardness of water

20 cm³ of sample (V_{sample}) was transferred to a titration vessel and 2 cm³ of the ammonia buffer solution and a bit of indicator ET-00 were added. The obtained violet solution was titrated with the EDTA standard solution until the color of the solution had turned to a stabile blue. all in all 6 titrations were carried out for the determination of water hardness.

Model Equation:

{The main equation}

$$x = (1000 * V_{EDTA\_sample} * c_{EDTA} * R) *2/ V_{sample};$$

{Determination of the concentration of the titrant (EDTA standard solution)}

$$c_{EDTA} = c_{MgSO4} * V_{MgSO4} * R_{EDTA} / V_{EDTA\_stand};$$

{Uncertainty of the volume of $MgSO_4$ standard substance solution}

$$V_{MgSO4} = V_{MgSO4\_rep} + V_{MgSO4\_cal} + V_{MgSO4\_tem};$$

$$V_{MgSO4\_tem} = V_{MgSO4\_cal} * \Theta * \gamma;$$

{Uncertainty of the volume of EDTA standard solution in the case of standardization}

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$V_{EDTA\_stand} = V_{EDTA\_rep} + V_{EDTA\_tem} + V_{EDTA\_end}$;

$V_{EDTA\_tem} = V_{EDTA\_rep} * \Theta * \gamma$;

$R_{EDTA} = V_{EDTA\_rep} / const(V_{EDTA\_rep})$;

{Uncertainty of the volume of EDTA standard solution needed for the titration of sample solution }

$V_{EDTA\_sample} = V_{EDTA\_rep\_sample} + V_{EDTA\_tem\_sample} + V_{EDTA\_end\_sample}$;

$V_{EDTA\_tem\_sample} = V_{EDTA\_rep\_sample} * \Theta * \gamma$;

$R = V_{EDTA\_rep\_sample} / const(V_{EDTA\_rep\_sample})$;

{Uncertainty of the volume of sample solution}

$V_{sample} = V_{rep\_sample} + V_{tem\_sample} + V_{cal\_sample}$;

$V_{tem\_sample} = V_{rep\_sample} * \Theta * \gamma$;

List of Quantities:

Quantity	Unit	Definition
x	mg-eqv/l	Total hardness of water
V_{EDTA_sample}	ml	Volume of the EDTA standard solution needed for the titration of the sample
c_{EDTA}	mol/l	Concentration of the EDTA standard solution
R	unitless	Recovery factor of the sample analysis
V_{sample}	ml	Volume of the pipette used for measuring the sample
c_{MgSO4}	mol/l	Concentration of the $MgSO_4$ standard substance solution
V_{MgSO4}	ml	Volume of the $MgSO_4$ standard substance solution taken for the titration of the EDTA standard solution
R_{EDTA}	unitless	Recovery factor of the standardization of the EDTA standard solution
V_{EDTA_stand}	ml	Volume of the EDTA standard solution needed for the titration of $MgSO_4$ standard substance solution
V_{MgSO4_rep}	ml	Repeatability uncertainty component of the 10 ml pipette used to measure the 10 ml aliquot of the $MgSO_4$ standard substance solution
V_{MgSO4_cal}	ml	Value and the calibration uncertainty component of the volume of the 10 ml pipette used to measure the 10 ml aliquot of the $MgSO_4$ standard substance solution
V_{MgSO4_tem}	ml	Temperature uncertainty component of the volume of the 10 ml pipette used to measure the 10 ml aliquot of the $MgSO_4$ standard substance solution

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Quantity	Unit	Definition
Θ	°C	Difference of the actual laboratory temperature from 20 degrees centigrade
γ	1/°C	The coefficient of volume expansion for water
V_{EDTA_rep}	ml	Value and the repeatability unceratinty component of the volume of EDTA standard solution needed for the titration of $MgSO_4$ primary standard solution (replicate tests)
V_{EDTA_tem}	ml	Temperature uncertainty component of the volume of EDTA standard solution needed for the titration of $MgSO_4$ primary standard solution
V_{EDTA_end}	ml	The end-point detrmination uncertainty component of the volume of EDTA standard solution needed for the titration of $MgSO_4$ primary standard solution
$V_{EDTA\_rep\_sample}$	ml	Value and the repeatability uncertainty component of the volume of the EDTA standard solution needed for the titration of sample (replicate tests)
$V_{EDTA\_tem\_sample}$	ml	Temperature uncertainty component of the volume of EDTA standard solution needed for the titration of sample solution
$V_{EDTA\_end\_sample}$	ml	The end-point determination uncertainty component of the volume of EDTA standard solution needed for the titration of sample solution
V_{rep_sample}	ml	Value and the repeatability uncertainty component of the 20 ml pipette with which the sample solution was measured for the analysis
V_{tem_sample}	ml	Temperature uncertainty component of the 20 ml pipette with which the sample solution was measured for the analysis
V_{cal_sample}	ml	Calibration uncertainty component of the 20 ml pipette with which the sample solution was measured for the analysis

x: Result

V_{EDTA_sample}: Interim Result

c_{EDTA}: Interim Result

R: Interim Result

V_{sample}: Interim Result

c_{MgSO4}: Type B normal distribution
Value: 0.05 mol/l
Expanded Uncertainty: 0.00007 mol/l
Coverage Factor: 1

V_{MgSO4}: Interim Result

R_{EDTA}: Interim Result

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V_{EDTA_stand}: Interim Result

V_{MgSO4_rep}: Type B normal distribution
Value: 0 ml
Expanded Uncertainty: 0.04 ml
Coverage Factor: 1

Estimate of uncertainty due to repeatability of volume of $MgSO_4$ primary standard solution is taken as 0.4% of the volume of the pipette.

V_{MgSO4_cal}: Type B rectangular distribution
Value: 10 ml
Halfwidth of Limits: 0.003 ml

V_{MgSO4_tem}: Interim Result

Θ: Type B rectangular distribution
Value: 0 °C
Halfwidth of Limits: 4 °C

γ: Constant
Value: 0.00021 1/°C

V_{EDTA_rep}: Type A
Method of observation: Direct
Number of observations: 4

No.	Observation
1	24.42
2	24.39
3	24.42
4	24.40

Arithmetic Mean: 24.40750 ml
Standard Deviation: 0.015 ml
Standard Uncertainty: 0.00750 ml
Degrees of Freedom: 3

V_{EDTA_tem}: Interim Result

V_{EDTA_end}: Type B normal distribution
Value: 0 ml
Expanded Uncertainty: 0.03 ml
Coverage Factor: 1

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$V_{EDTA\_rep\_sample}$: Type A
Method of observation: Direct
Number of observations: 6

No.	Observation
1	6.19
2	6.17
3	6.18
4	6.22
5	6.23
6	6.21

Arithmetic Mean: 6.20000 ml
Standard Deviation: 0.024 ml
Standard Uncertainty: 0.00966 ml
Degrees of Freedom: 5

$V_{EDTA\_tem\_sample}$: Interim Result

$V_{EDTA\_end\_sample}$: Type B normal distribution
Value: 0 ml
Expanded Uncertainty: 0.05 ml
Coverage Factor: 1

The endpoint detection uncertainty is estimated slightly larger for the sample than for the titrant standardisation.

V_{rep_sample}: Type B normal distribution
Value: 0 ml
Expanded Uncertainty: 0.08 ml
Coverage Factor: 1

Estimate of uncertainty due to repeatability of volume of $MgSO_4$ primary standard solution is taken as 0.4% of the volume of the pipette.

V_{tem_sample}: Interim Result

V_{cal_sample}: Type B rectangular distribution
Value: 20 ml
Halfwidth of Limits: 0.06 ml

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Uncertainty Budget:

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
c_{MgSO4}	0.0500000 mol/l	$70.0 \cdot 10^{-6}$ mol/l	normal	250	0.018 mg-eqv/l	1.7 %
V_{MgSO4_rep}	0.0 ml	0.0400 ml	normal	1.3	0.051 mg-eqv/l	14.1 %
V_{MgSO4_cal}	10.00000 ml	0.00173 ml	rectangular	1.3	0.0022 mg-eqv/l	0.0 %
Θ	0.0 °C	2.31 °C	rectangular	0.0027	0.0062 mg-eqv/l	0.2 %
γ	0.00021 1/°C					
V_{EDTA_rep}	24.40750 ml	0.00750 ml	normal	0.0	0.0 mg-eqv/l	0.0 %
V_{EDTA_end}	0.0 ml	0.0300 ml	normal	-0.52	-0.016 mg-eqv/l	1.3 %
$V_{EDTA\_rep\_sample}$	6.20000 ml	0.00966 ml	normal	4.1	0.040 mg-eqv/l	8.6 %
$V_{EDTA\_end\_sample}$	0.0 ml	0.0500 ml	normal	2.0	0.10 mg-eqv/l	57.3 %
V_{rep_sample}	0.0 ml	0.0800 ml	normal	-0.64	-0.051 mg-eqv/l	14.1 %
V_{cal_sample}	20.0000 ml	0.0346 ml	rectangular	-0.64	-0.022 mg-eqv/l	2.6 %
x	12.701 mg-eqv/l	0.135 mg-eqv/l				

Result: Quantity: x
Value: 12.70 mg-eqv/l
Expanded Uncertainty: ±0.27 mg-eqv/l
Coverage Factor: 2.00
Coverage: manual

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