Determination of total water hardness via chelatometry

Task:
Determine in $mmol.l^{-1}$ the total water hardness; determine in $mg.l^{-1}$ the calcium and magnesium content in drinking water.

Principle:
The total water hardness is caused not only by Ca^{2+} a Mg^{2+} salts contained in water, but by Sr^{2+} and Ba^{2+} as well. Their presence depends on the amount of dissolved CO_2, which balances the reaction:

$$CaCO_3 + CO_2 + H_2O \longleftrightarrow Ca^{2+} + 2HCO_3^-$$

Water hardness is determined via direct titration of volumetric solution chelaton 3 in the dampening ammonia solution using the Eriochromium black T indicator.

Reaction equation:

$$Ca^{2+} + H_2Y^{2-} \xrightarrow{ECHCT} CaY^{2-} + 2H^+$$
$$Mg^{2+} + H_2Y^{2-} \xrightarrow{ECHCT} MgY^{2-} + 2H^+$$

If we want to determine Ca^{2+} only, we titrate it using murexid or fluorexon indicator at 12 - 13 pH. At this pH, the concurrently present Mg^{2+} ions condense as $Mg(OH)_2$ (↓ white) so only $Ca^{2+}$is titrated. We calculate the amount of Mg^{2+} in the sample according to the difference in volume of a volumetric solution / murexid.

Tools:
Titration flasks, burette, pipette (100 ml), graduated cylinder (5 ml).

Chemicals:
Chelaton 3 o c= 0.05 $mol.l^{-1}$, Eriochromium black T, dampening ammonia solution.

Sample:
Drinking water.

Procedure:
1) Prepare 250 ml of chelaton 3 volumetric solution with the concentration of 0.05 $mol.l^{-1}$.
2) Calculate the real concentration of chelaton 3 from its real weight.
3) Pipette 100 ml of tested water into a titration flask.
4) Add 5 ml of dampening ammonia solution by a graduated cylinder.
5) Add a small amount of Eriochromium black T and titrate from wine red to blue colouring which lasts for 1 min.
6) Determine 3x. Calculate water hardness in $mmol.l^{-1}$.

Assessment:
Calculation:
Weight of chelaton 3:
m (g)= c * V * M (the volume in litres)

The real concentration of chelaton 3:
c (real) = c (theoretical) * m (real) / m (theoretical)

Calculation of total water hardness c in mmol.l^{-1}:

$$c = \frac{c_{CH3}.V_{CH3}}{V_{water}}.1000$$

where: c_{CH3} – concentration of chelaton 3 in mol.l^{-1}
V_{CH3} – consumption of chelaton 3 in ml
V_{water} – volume of water sample in ml

In the past, water hardness was determined in German degrees ^{0}N, when:
1 ^{0}N = 1 mg CaO /100 ml water and **1 mmol.l^{-1} = 5.6^{0}N**

Tab. 1: Types of water according to hardness

Water hardness	**Water hardness in mmol.l^{-1}**	**Water hardness in ^{0}N**
Very soft	0 – 0.7	0 - 4
Soft	0.7 – 1.4	4 – 8
Medium soft	1.4 – 2.1	8 - 12
Quite hard	2.1 – 3.2	12 – 18
Hard	3.2 – 5.4	18 – 30
Very hard	> 5.4	> 30

Ministry of Health Regulation 252/2004 suggests drinking water hardness 2-3.5 mmol.l^{-1} (11.2 ^{0}N – 19.6^{0}N).

Determination of Ca^{2+}

Principle:
Calcium is a natural part of water contributing to its hardness. Ca^{2+} is titrated by volumetric solution chelaton 3 using murexid indicator in the diluted NaOH at pH 12.

$$Ca^{2+} + H_2Y^{2-} \xrightarrow{murexid} CaY^{2-} + 2H^+$$

Tools:
Titration flasks, pipettes (100 ml, 2 ml), graduated cylinder (100 ml), burette.

Chemicals:
NaOH (c= 0.1 mol.l^{-1}), HCl (c= 0.1 mol.l^{-1}), NaOH (c= 5 mol.l^{-1}), murexid, chelaton 3 (c= 0.05 mol.l^{-1}).

Procedure:
Pipette 100 ml of water sample into a titration flask. Add 2 ml 5 M NaOH, murexid indicator and titrate by 0.05 M chelaton 3 to blue-violet colouring.

Assessment:
Calculate the amount of Ca^{2+} in mol.l^{-1} or in mg.l^{-1}.

Determination of Mg^{2+}

Magnesium causes water hardness. We determine it via complexometry or by calculating the difference of consumption using Eriochromium black T and murexid.

Assessment:

$V(Mg^{2+}) = V(\text{water hardness}) - V(Ca^{2+})$