

Article

A Paper-Based Potentiometric Platform for Determination of Water Hardness

Mohammed L. Bouhoun ^{1,2}, Pascal Blondeau ¹, Yamina Louafi ² and Francisco J. Andrade ^{1,*}

¹ Department of Analytical and Organic Chemistry, Universitat Rovira i Virgili, 43007 Tarragona, Spain; bouhoun-m-l@hotmail.fr (M.L.B.); pascal.blondeau@urv.cat (P.B.)

² Laboratory of Electrochemistry-Corrosion, Metallurgy and Inorganic Chemistry, Faculty of Chemistry, U.S.T.H.B., BP 32, Algiers 16111, Algeria; amina.elouafi@yahoo.fr

* Correspondence: franciscojavier.andrade@urv.cat

Citation: Bouhoun, M.L.; Blondeau, P.; Louafi, Y.; Andrade, F.J. A Paper-Based Potentiometric Platform for Determination of Water Hardness. *Chemosensors* **2021**, *9*, 96. <https://doi.org/10.3390/chemosensors9050096>

Academic Editors: Sam F. Y. Li and Alain Walcarius

Received: 10 March 2021

Accepted: 25 April 2021

Published: 28 April 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).

Table S1. Classification of water quality according to the total hardness.

Water type	Water hardness (mg L ⁻¹ CaCO ₃)
Soft	0–50
Moderately soft	50–100
Slightly hard	100–150
Moderately hard	150–250
Hard	250–350
Very hard	350<

Table S2. Mg²⁺, Ca²⁺ Ion selective and reference membranes composition respectively.

Mg ²⁺ Membrane		wt %
Ion exchanger	Potassium tetrakis(4-chlorophenyl)-borate	0.76
Ionophore	Magnesium ionophore VI	1.03
Matrix	PVC (81387)	30.93
Plasticizer	o-NPOE	67.28
Solvent	THF	1 mL

Ca ²⁺ Membrane		wt %
Ion exchanger	Potassium tetrakis(4-chlorophenyl)-borate	0.60
Ionophore	Calcium ionophore II (ETH 129)	1.00
Matrix	PVC (81387)	32.80
Plasticizer	o-NPOE	65.60
Solvent	THF	1 mL

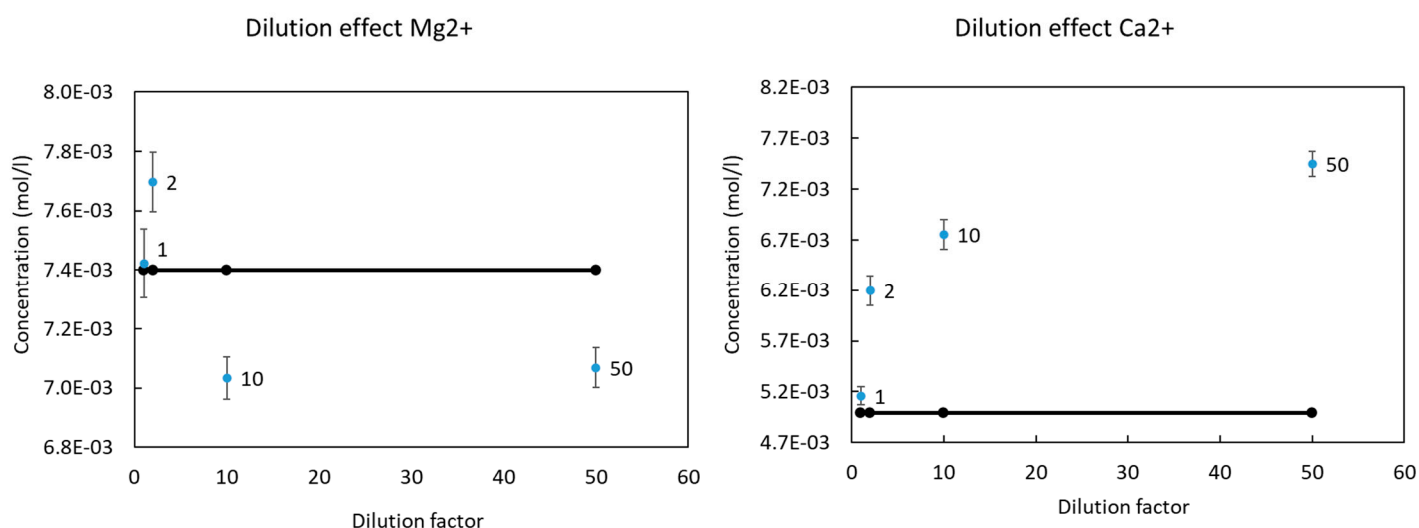
Reference Membrane	Quantity
Polyvinyl butyral (PVB)	78 mg
Sodium chloride (NaCl)	50 mg
Methanol	1 mL

Table S3. Analytical parameters of calcium and magnesium paper-based ISEs in a separate calibration.

	Ca ²⁺ separately	Mg ²⁺ separately
Sensitivity	27.0 ± 0.07	30.9 ± 0.03
Linear range	10 ⁻⁶ –10 ⁻¹	10 ⁻⁶ –10 ⁻¹
Detection limit	3.3 × 10 ⁻⁷	3.6 × 10 ⁻⁷

Table S4. The chemical composition of the artificial water samples with chloride as counter anion.

Samples	Concentration (mol/l)			
	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
1	5.24E-04	2.06E-04	3.91E-04	3.58E-05
2	1.80E-04	6.17E-05	1.74E-04	5.12E-05
3	7.76E-04	2.30E-04	2.35E-04	4.35E-05
4	4.59E-04	2.30E-04	2.39E-04	9.72E-05
5	3.12E-04	1.56E-04	4.78E-04	1.00E-04
6	9.73E-05	1.11E-04	1.26E-04	3.58E-05
7	3.74E-04	1.69E-04	2.74E-04	5.88E-05
8	1.87E-03	2.06E-03	4.00E-04	1.00E-04
9	4.99E-03	6.17E-03	4.00E-04	1.00E-04
10	1.00E-03	1.00E-03	4.00E-04	1.00E-04
11	1.00E-04	7.40E-03	4.00E-04	1.00E-04

**Figure S1.** The dilution effect on the prediction of Mg²⁺ and Ca²⁺ sensors respectively (N = 3).**Table S5.** Prediction of Ca²⁺ and Mg²⁺ in artificial water samples.

a) Separated measurements (N = 3)

Sample N°	Log a (Mg 2+)			
	Average	SD	Expected	Recover
1	-3.75	0.03	-3.69	-0.02
2	-4.34	0.05	-4.21	-0.03
3	-3.78	0.04	-3.64	-0.04
4	-3.77	0.11	-3.64	-0.04
5	-3.92	0.11	-3.81	-0.03
6	-4.05	0.10	-3.95	-0.02
7	-3.85	0.09	-3.77	-0.02
8	-2.71	0.05	-2.69	-0.01
10	-2.99	0.05	-3.00	0.00

Log a (Ca 2+)				
Sample N°	Average	SD	Expected	Recover
1	−3.34	0.04	−3.28	−0.02
2	−3.87	0.05	−3.75	−0.03
3	−3.26	0.04	−3.11	−0.05
4	−3.49	0.04	−3.34	−0.04
5	−3.54	0.02	−3.51	−0.01
6	−4.04	0.03	−4.01	−0.01
7	−3.48	0.03	−3.43	−0.01
8	−2.83	0.01	−2.73	−0.04
10	−3.11	0.01	−3.00	−0.04
Total hardness as of CaCO ₃ mg L ^{−1}				
Sample N°	Average	SD	Expected	Recover
1	63.40	2.96	72.97	0.13
2	18.31	1.02	24.14	0.24
3	72.36	3.91	100.64	0.28
4	50.18	1.60	68.95	0.27
5	41.51	3.55	46.82	0.11
6	18.23	2.09	20.84	0.13
7	47.79	3.40	54.30	0.12
8	344.68	17.70	392.85	0.12
10	180.87	10.87	200.00	0.10

Total hardness is given as CaCO₃ (mg L^{−1}) by the equation:

$$^{\circ}\text{TH} = ([\text{Ca}^{2+}] + [\text{Mg}^{2+}]) / (10^{-5})$$

where $[\text{Ca}^{2+}] + [\text{Mg}^{2+}]$ represents the sum of the molar concentrations of these ions.

b) Simultaneous measurements (N = 3).

Log a (Mg 2+)				
Sample N°	Average	SD	Expected	Recover
1	−3.71	0.05	−3.69	−0.01
4	−3.59	0.03	−3.64	0.01
5	−3.75	0.03	−3.81	0.01
6	−3.95	0.04	−3.95	0.00
7	−3.77	0.04	−3.77	0.00
10	−3.01	0.01	−3.00	0.00

Log a (Ca2+)				
Sample N°	Average	SD	Expected	Recover
1	−3.30	0.12	−3.28	−0.01
4	−3.16	0.11	−3.34	0.05
5	−3.35	0.11	−3.51	0.05
6	−3.83	0.11	−4.01	0.05
7	−3.35	0.11	−3.43	0.02

10	−2.94	0.01	−3.00	0.02
----	-------	------	-------	------

Total hardness as of CaCO ₃ mg L ^{−1}				
Sample N°	Average	SD	Expected	Recover
1	69.55	11.18	72.97	0.05
4	95.25	15.54	68.95	−0.38
5	62.76	9.84	46.82	−0.34
6	26.11	2.91	20.84	−0.25
7	62.18	9.23	54.30	−0.15
10	214.10	0.21	200.00	−0.07

Reference

- [1] Abeliotis, K.; Candan, C.; Amberg, C.; Ferri, A.; Osset, M.; Owens, J.; Stamminger, R. Impact of water hardness on consumers' perception of laundry washing result in five European countries, *Int. J. Consum. Stud.* **2015**, *39*, 60–66, doi: 10.1111/ijcs.12149.