Electronic Supplementary Material (ESI) for Analytical Methods.

A novel voltammetric method for the sensitive and selective determination of carbonate or bicarbonate ions by an azomethine-H probe

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1. Experimental

Materials and methods

Azomethine-H monosodium salt hydrate (Sigma-Aldrich 11635 p.a.), sodium carbonate (Merck 1.06392) and sodium bicarbonate (Merck 1.06329) were supplied from Sigma-Aldrich, while all other chemicals were analytical reagent grade. The Milli-Q Direct 8 water purification system was used to obtain ultrapure water for the preparation of solutions. All solutions were stored in high-density polyethylene (HDPE) Falcon tubes and bottles.

Voltammetric measurements were performed with the Metrohm Autolab PGSTAT 128N involving a pencil graphite electrode (ONAS MP 775 body with Tombow 0.5-mm H pencil graphite, surface area: 15.90 mm^2, immersion depth: 1 cm) as a working electrode, platinum wire (BASi MW-1032, 7.5 cm) as a counter electrode and Ag/AgCl with 3 M NaCl (BASi MF-2052 RE-5B) as a reference electrode. Different types of Tombow pencil graphite were obtained from a stationer.

An auto-titration system (Metrohm 916 Ti-touch) involving the combined pH electrode (Metrohm iEcotrode plus), potentiometer, magnetic stirrer and high-accuracy dosing unit was used to determine carbonate or bicarbonate ingredients in the samples. Meanwhile, the Varian Cary Eclipse Fluorescence spectrophotometer and Varian VNMRS-600 ^{1}H-NMR were used to determine the complex stoichiometry between azomethine-H and carbonate or bicarbonate ions.

A desktop pH measurement system (Mettler Toledo Seven Compact pH meter and InLab Expert Pro-ISM combined pH electrode) with a thermostatic circulating bath (Thermo Haake DC 10 K20) was used to prepare buffer solutions.

Voltammetric measurement

A disposable pencil graphite electrode was used in voltammetric measurements without any preprocessing. Synthetic or real samples were transferred into the 1 mM **AH** solution and stirred for 30 s before the measurement, then differential pulse voltammetry was used to determine carbonate or bicarbonate ions in 0.09 M acetic acid–acetate buffer (pH: 4.25) solution. Argon gas was passed through the solution to remove the dissolved gases and, in turn, over the solution to prevent their re-dissolution. The instrumental parameters of step amplitude, pulse amplitude, interval time and pulse time used were 10 mV, 80 mV, 0.10 s and 0.09 s, respectively, and the potential was ranged from 0.2 V to -1.6 V. The measurements were carried out at (21 ± 3) °C and (45 ± 15)% relative humidity.

Potentiometric titration

A titrant solution of approximately 0.1 mol/L HCl was prepared and adjusted with Tris. Samples properly diluted with ultrapure water were directly titrated to the first point of equivalence by an adjusted HCl solution.

Fluorescence measurement

Solutions containing different ratios of bicarbonate ion and **AH** in acetic acid/acetate buffer solution (pH: 4.25) were prepared so that the total number of moles was 2×10^{-5}, and the ratio of the complex between **AH** and bicarbonate ion was determined by creating a Job plot based on the fluorescence intensity changing of the complex. Fluorescence measurements were performed with a quartz cuvette with a 10.0 mm path length and 2.0 mL of sample volume. Both slit widths for excitation and emission were 5 nm. The emission spectra were examined within the range of 355 nm–700 nm, with excitation at 345 nm.

^{1}H-NMR titration

A series of ^{1}H-NMR titration studies was performed in a 15 mg/mL **AH** solution with the addition of proportional amounts of carbonate or bicarbonate ions. **AH** and carbonate derivatives were prepared in D_2O. ^{1}H-NMR spectra were interpreted to enlighten the complex formation and stoichiometry.

Sample preparation procedure

The tap, drinking and sparkling water samples and baking powder were sourced from the district of Gebze, in Kocaeli Province in Turkey. The seawater sample was collected from Eskihisar beach of Marmara Sea in Kocaeli. The tap and drinking water samples were prepared by dissolving approximately 1.25 g sodium carbonate in 250 mL of these water samples. This was performed due to the low sensitivity of the titrimetric method and in order to compare the results of potentiometric titrimetry and voltammetry. About 1 g of baking powder was weighed and diluted with ultrapure water to 250 mL. The pH values of the samples were adjusted to 12.5 (99.33% of carbonate) for carbonate determination and to 8.35 (98.00% of bicarbonate) for bicarbonate determination, and the samples were transferred into the 1 mM **AH** solution and stirred for 30 s before the measurement. 10 mL of spiked tap or spiked-drinking water samples, 20 mL of sparkling water samples, 200 mL of seawater samples, and 10 mL of prepared baking powder solution were used to determine the carbonate or bicarbonate amounts of the samples using potentiometric titration. The dilution factors were determined so that the final carbonate or bicarbonate concentrations in the samples were 300 µg/L for voltammetric measurements.

2. Voltammetric behaviour of the azomethine-H and carbonate system

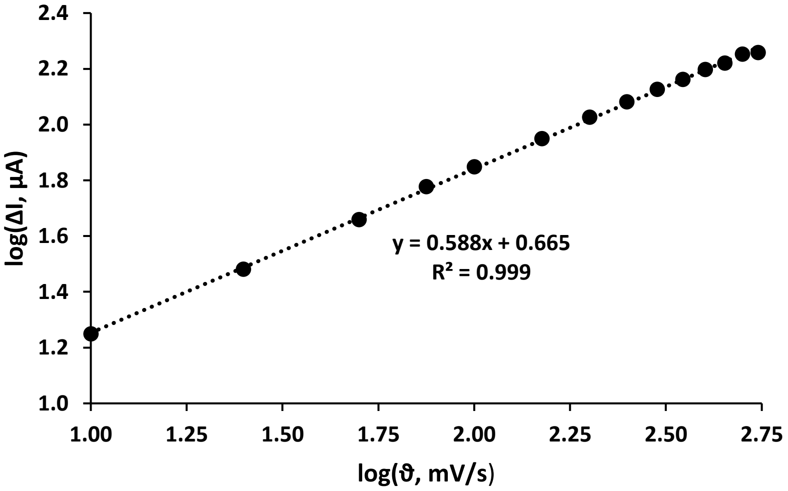


Fig. S1. $\log(\Delta I) - \log(\vartheta)$ plot for **AH** and carbonate system. Conditions: 1 mM **AH** and 1.5 mg/L carbonate in 0.09 M acetic acid/acetate buffer (pH: 4.25). E_{start}: -1.6 V, E_{first}: 0.2 V and E_{finish}: -1.6 V.

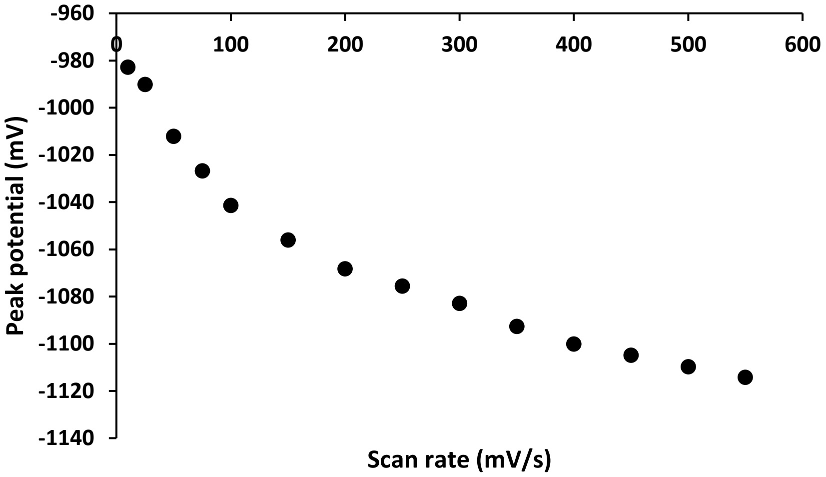


Fig. S2. Peak potential – scan rate plot for **AH** and carbonate system. Conditions: 1 mM **AH** and 1.5 mg/L carbonate in 0.09 M acetic acid/acetate buffer (pH: 4.25). E_{start}: -1.6 V, E_{first}: 0.2 V and E_{finish}: -1.6 V.

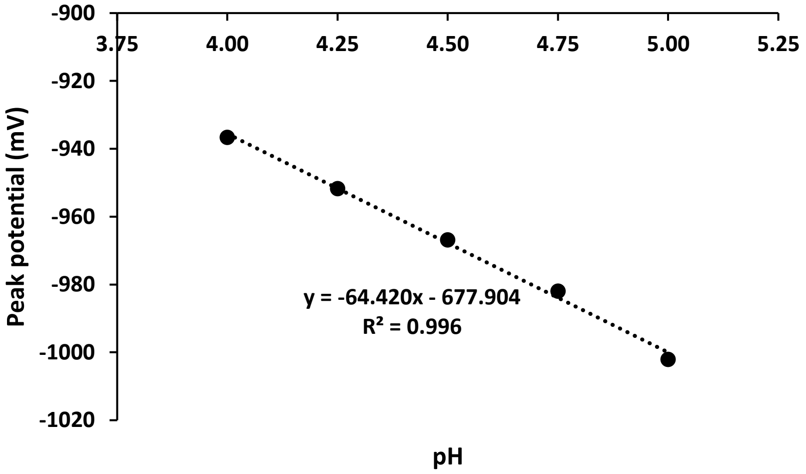


Fig. S3. Peak potential – pH plot for **AH** and carbonate system. Conditions: 1 mM **AH** and 0.3 mg/L carbonate in 0.09 M acetic acid/acetate buffer solutions. E_{start}: -1.6 V, E_{first}: 0.2 V, E_{finish}: -1.6 V and 2.5 mV of step amplitude.

3. Complex stoichiometry and electrochemical reaction mechanism

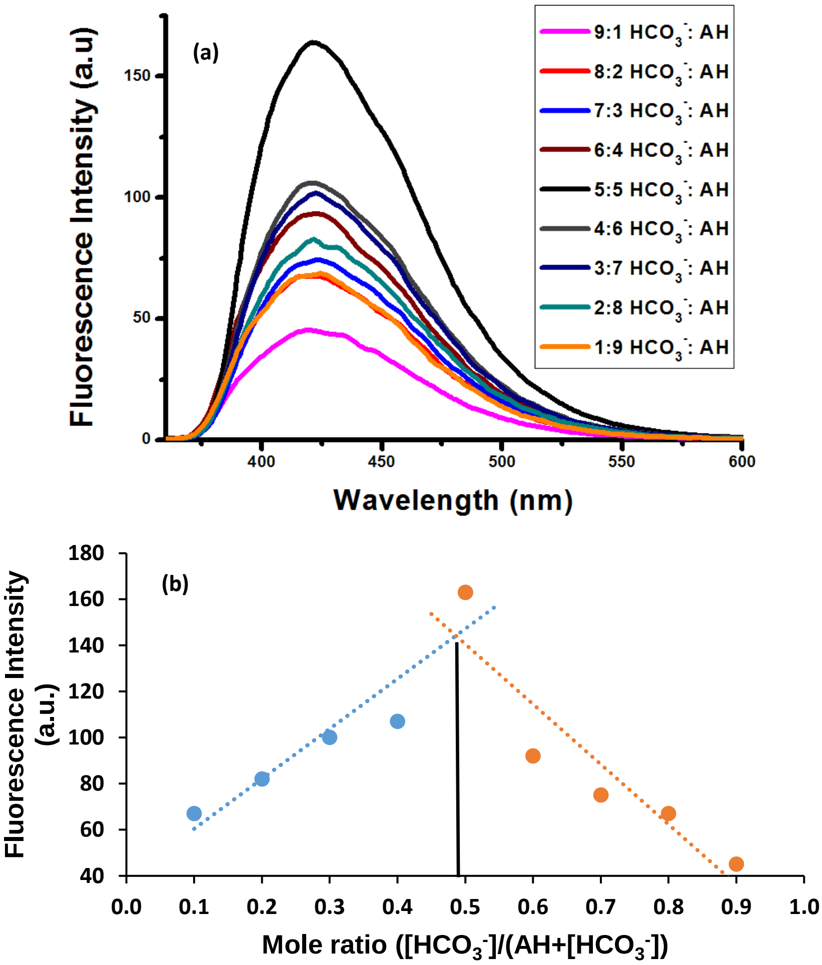


Fig. S4. (a) Fluorescence spectra and (b) Job plot for **AH** and bicarbonate system. Conditions: path length: 10.0 mm, sample volume: 2.0 mL, slit widths for excitation and emission: 5 nm, emission measurement range: 355 nm–700 nm and excitation wave length: 345 nm.

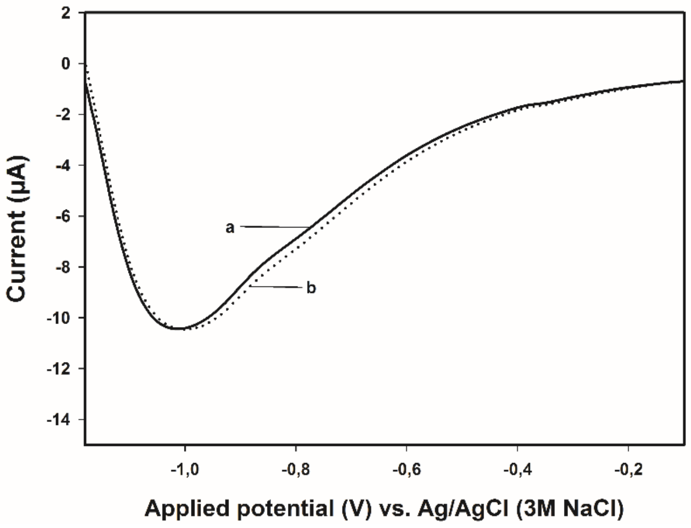


Fig. S5. The effect of carbonic acid. (a): 1 mM **AH** and (b): + 0.7 mg/L pH: 2 carbonic acid in 0.09 M acetic acid/acetate buffer solution (pH: 4.25). E_{start}: 0.2 V, E_{finish}: -1.6 V, pulse time: 0.09 s, interval time: 0.10 s, step amplitude: 10 mV, and pulse amplitude: 80 mV.

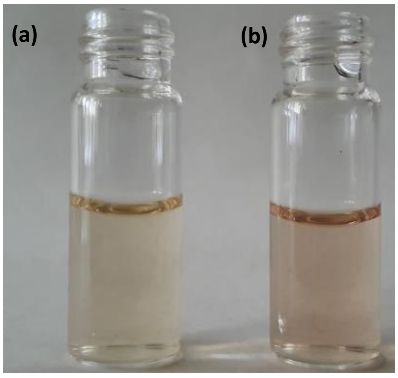


Fig. S6. The visible difference in daylight between (a) before addition and (b) after addition of carbonate into the **AH** solution.

4. Optimisation studies

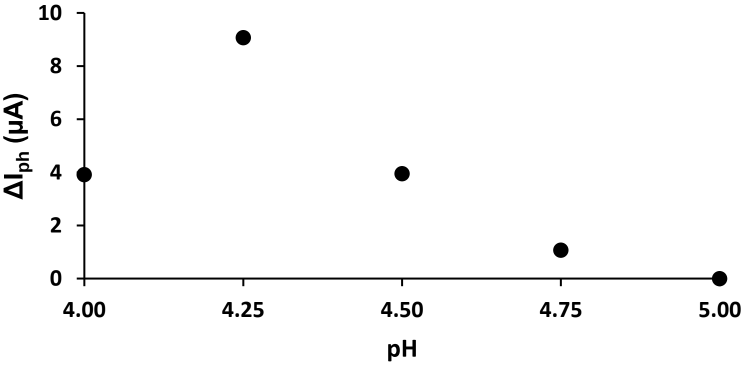


Fig. S7. The effect of pH on peak height. Conditions: 1 mM **AH** and 0.3 mg/L carbonate in 0.09 M acetic acid/acetate buffer solutions. E_{start}: 0.2 V, E_{finish}: -1.6 V, pulse time: 0.09 s, interval time: 0.10 s, step amplitude: 10 mV, and pulse amplitude: 80 mV.

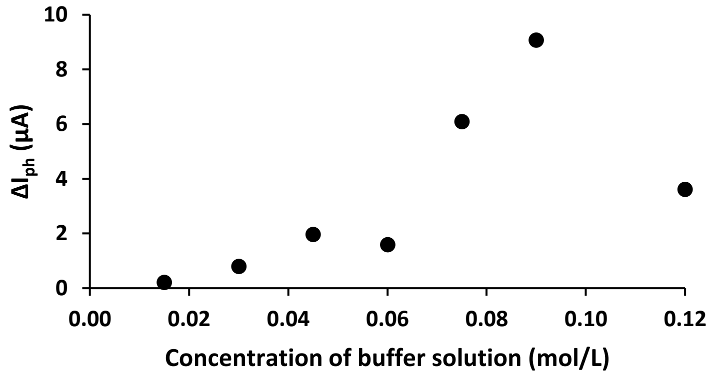


Fig. S8. The effect of concentration of buffer solution on peak height. Conditions: 1 mM **AH** and 0.3 mg/L carbonate in different concentrations of pH: 4.25 acetic acid/acetate buffer solution. E_{start}: 0.2 V, E_{finish}: -1.6 V, pulse time: 0.09 s, interval time: 0.10 s, step amplitude: 10 mV, and pulse amplitude: 80 mV.

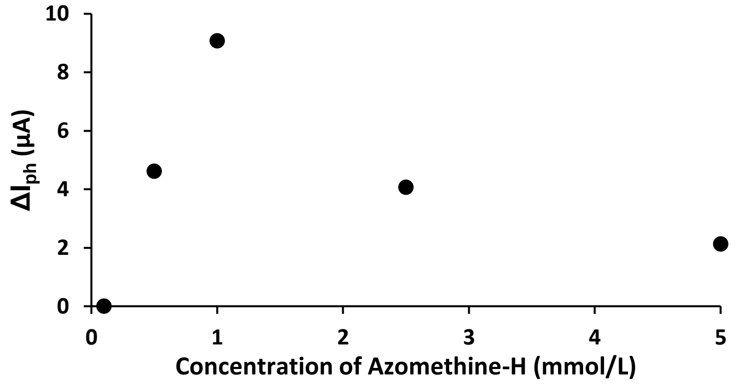


Fig. S9. The effect of concentration of **AH** on peak height. Conditions: Different concentrations of **AH** and 0.3 mg/L carbonate in 0.09 M acetic acid/acetate buffer solution (pH: 4.25). E_{start}: 0.2 V, E_{finish}: -1.6 V, pulse time: 0.09 s, interval time: 0.10 s, step amplitude: 10 mV, and pulse amplitude: 80 mV.

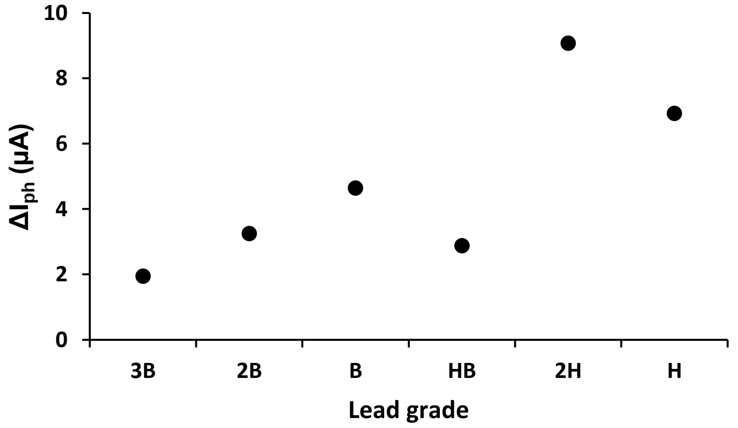


Fig. S10. The effect of lead grade on peak height. Conditions: 1 mM **AH** and 0.3 mg/L carbonate in 0.09 M acetic acid/acetate buffer solution (pH: 4.25). E_{start}: 0.2 V, E_{finish}: -1.6 V, pulse time: 0.09 s, interval time: 0.10 s, step amplitude: 10 mV, and pulse amplitude: 80 mV.

5. Method validation

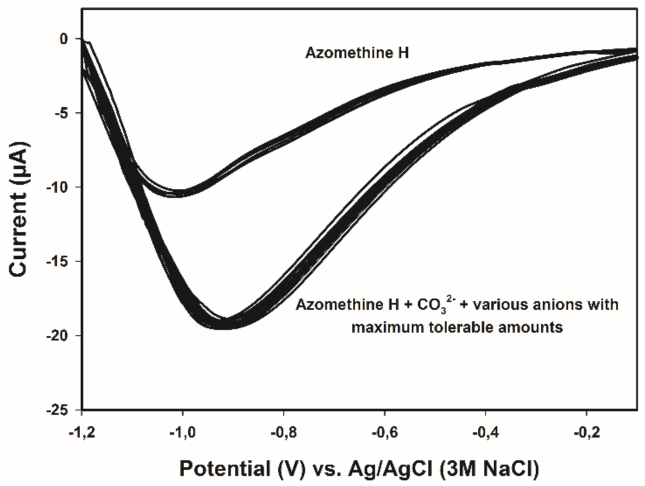


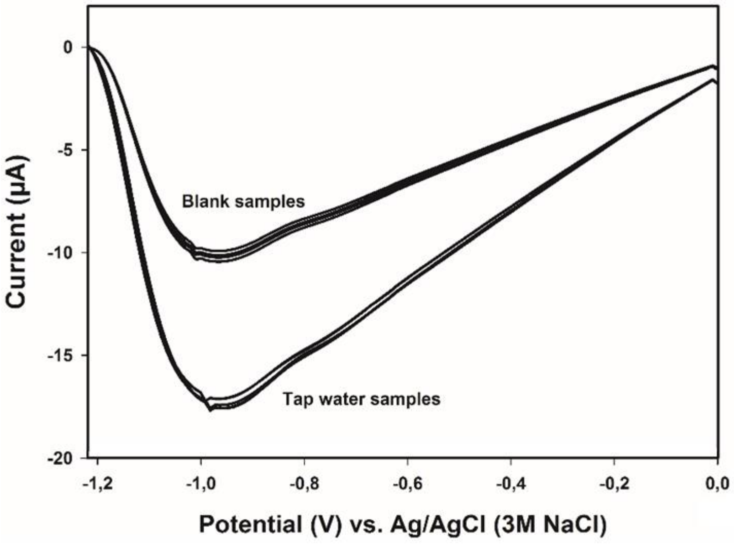
Fig. S11. The interference effects of anions Cl^-, Br^-, F^-, I^-, NO_3^-, NO_2^-, CH_3COO^-, CN^-, SO_4^{2-}, SO_3^{2-}, ClO_4^-, $H_2PO_4^-$, HPO_4^{2-}, N_3^-, S^{2-} and $S_2O_3^{2-}$. Conditions: 1 mM **AH**, 0.3 mg/L carbonate and maximum tolerable amounts of interference anions (as in Table S1) in 0.09 M acetic acid/acetate buffer solution (pH: 4.25). E_{start}: 0.2 V, E_{finish}: -1.6 V, pulse time: 0.09 s, interval time: 0.10 s, step amplitude: 10 mV, and pulse amplitude: 80 mV.

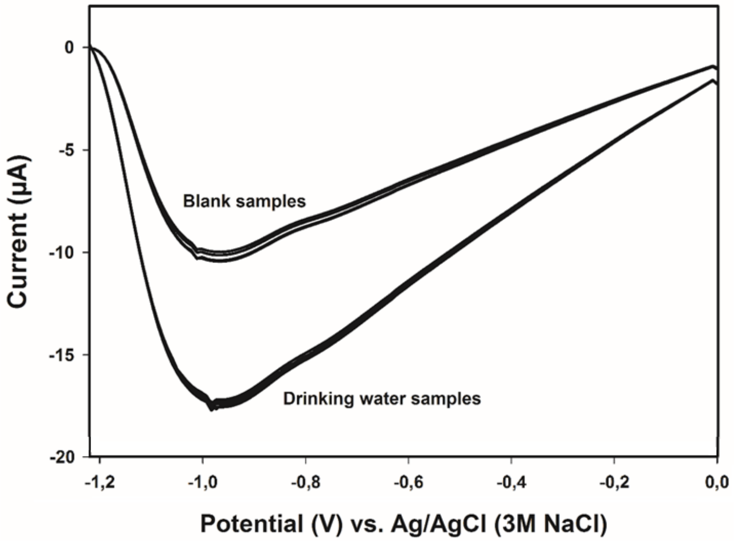
Table S1. Interference studies with tolerable ratios. Conditions: 1 mM **AH**, 0.3 mg/L carbonate and different amounts of interference anions in 0.09 M acetic acid/acetate buffer solution (pH: 4.25). E_{start}: 0.2 V, E_{finish}: -1.6 V, pulse time: 0.09 s, interval time: 0.10 s, step amplitude: 10 mV, and pulse amplitude: 80 mV.

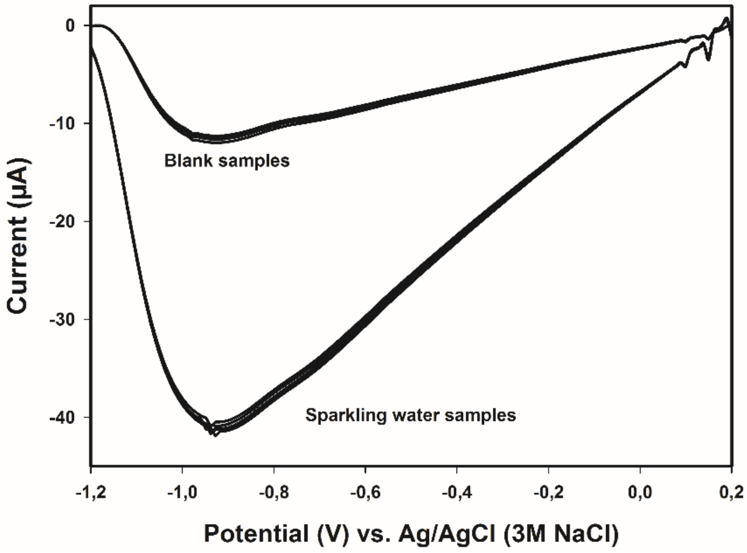
Interferences	Tolerable ratio[a]
F^-	1500
Cl^-, NO_3^-, SO_4^{2-}	1000
Br^-, NO_2^-	500
SO_3^{2-}, $S_2O_3^{2-}$	250
CN^-	100
HPO_4^{2-}	60
N_3^-	40
I^-	20
CH_3COO^-	16
$H_2PO_4^-$, ClO_4^-, S^{2-}	12

[a] The tolerable ratios of interference with a criterion of ±5.0% change in peak height belong to the mixture of 1 mM **AH** and 0.3 mg/L carbonate.

6. Sample application







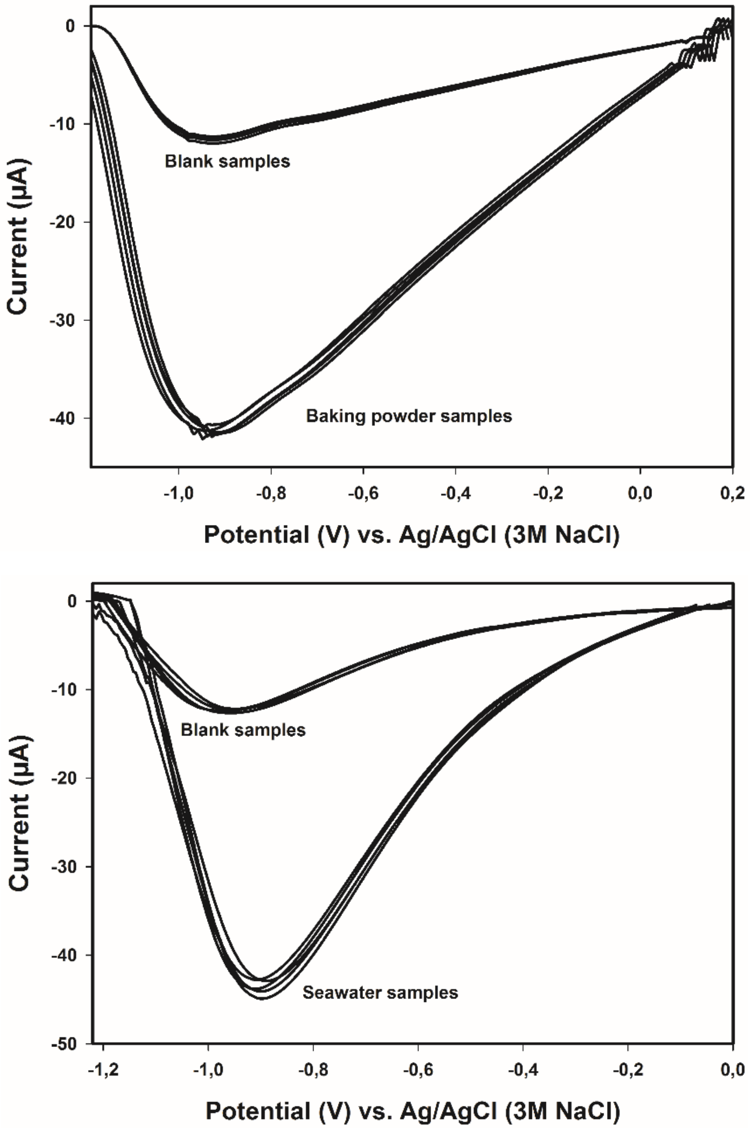
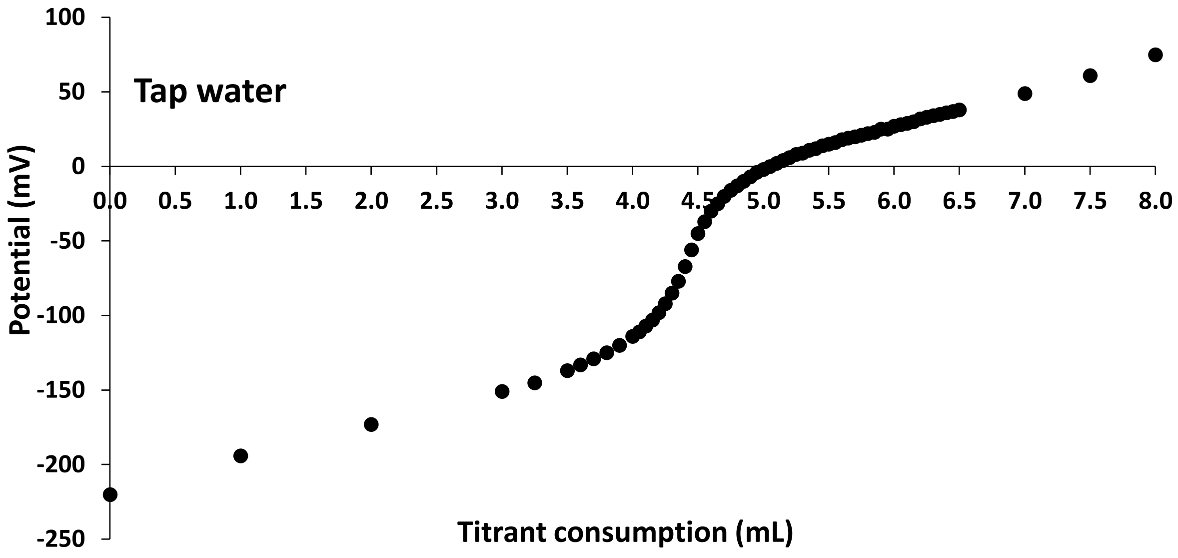
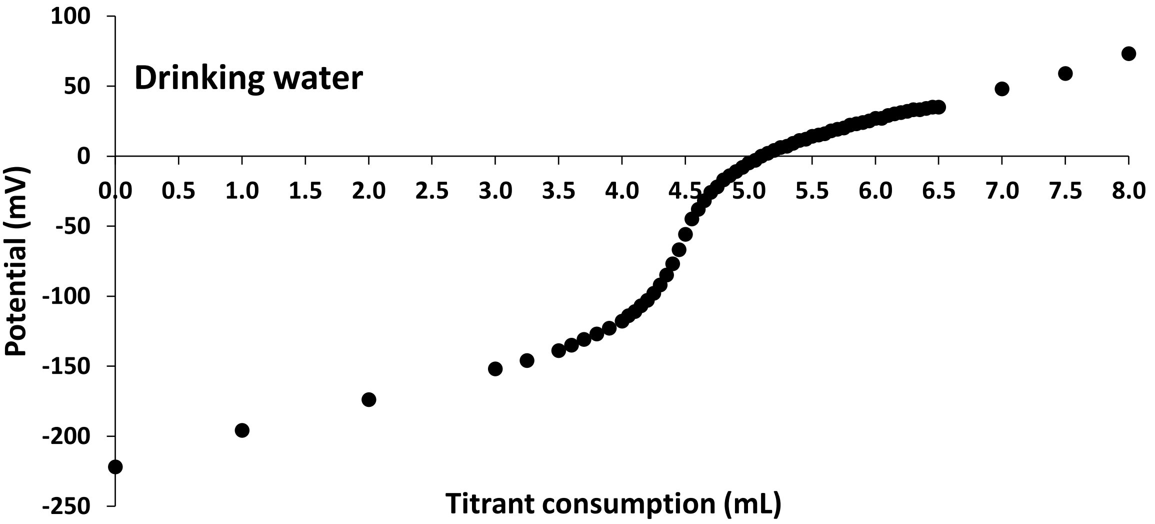
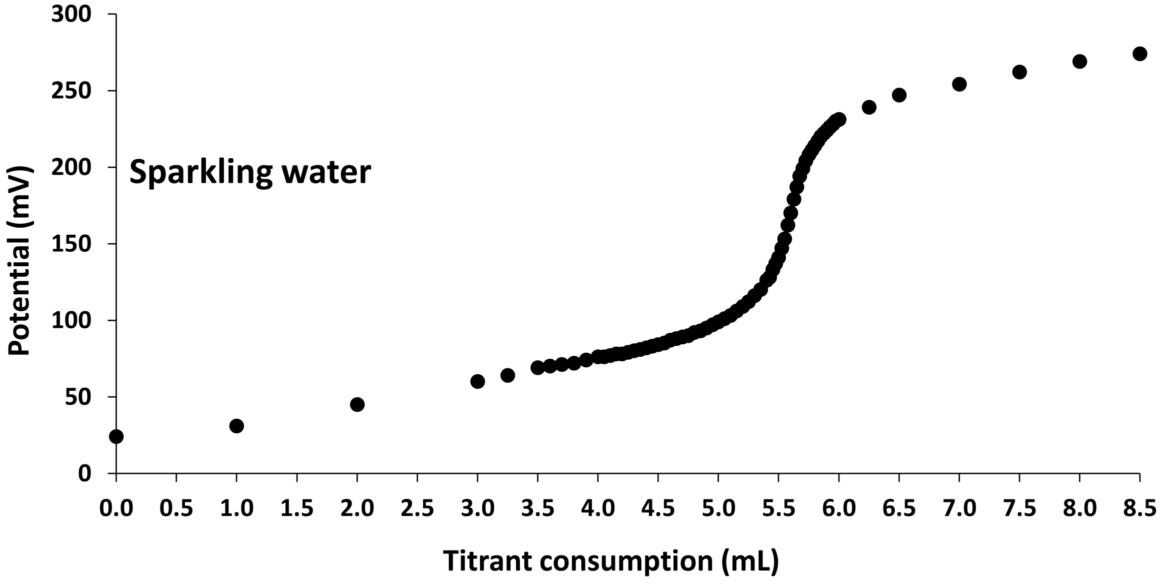


Fig. S12. The obtained voltammograms for tap, drinking and sparkling water, baking powder and seawater samples. Conditions: 1 mM **AH** and diluted amounts of real samples in 0.09 M acetic acid/acetate buffer solution (pH: 4.25). Blank sample: 1 mM **AH** in 0.09 M acetic acid/acetate buffer solution (pH: 4.25). Real sample: Blank sample + diluted amounts of real sample. E_{start}: 0.2 V, E_{finish}: -1.6 V, pulse time: 0.09 s, interval time: 0.10 s, step amplitude: 10 mV, and pulse amplitude: 80 mV. The pH values of the samples were adjusted to 12.5 for carbonate determination and to 8.35 for bicarbonate determination before the measurement.


Tap water
Potential (mV)
100
50
0
-50
-100
-150
-200
-250
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
Titrant consumption (mL)


Drinking water
Potential (mV)
100
50
0
-50
-100
-150
-200
-250
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
Titrant consumption (mL)


Sparkling water
Potential (mV)
300
250
200
150
100
50
0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
Titrant consumption (mL)

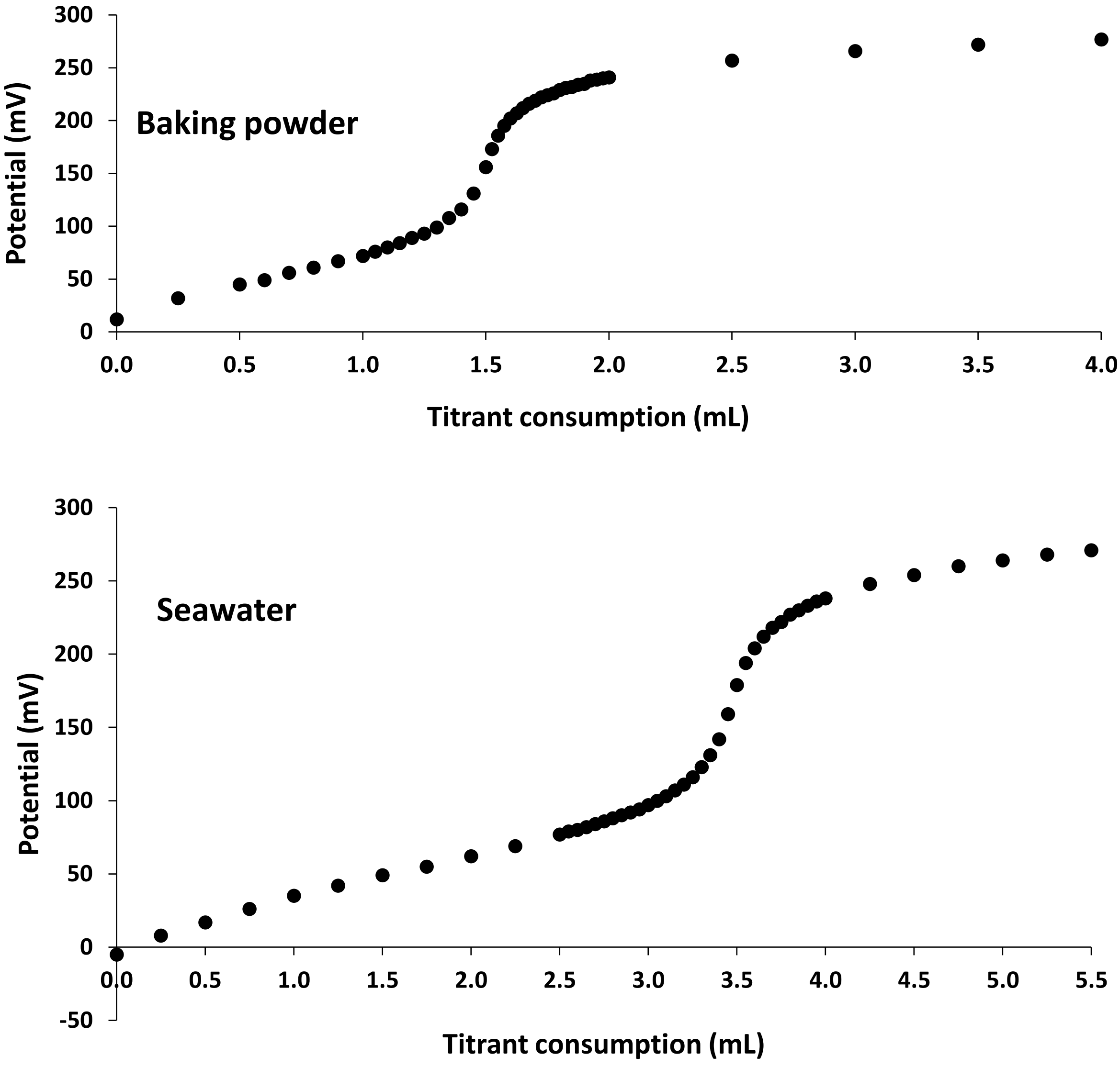


Fig. S13. The obtained titrimetric plots for diluted amounts of tap, drinking and sparkling water, baking powder and seawater samples. Titrant: 0.10553 mol/L HCl adjusted with Tris, indicator electrode: Metrohm iEcotrode plus pH electrode. (Single titrimetric plot for all samples was given here).

Table S2. Statistical evaluation of the results obtained from voltammetry and potentiometric titrimetry (n=5).

Sample	Bias (%)[a]	$t_{experimental}$[b]	$t_{critical}$[b]
Spiked-tap water	-0.19	0.09	2.57
Spiked-drinking water	0.06	0.03	2.78
Sparkling water	-0.67	0.53	2.57
Baking powder	-0.12	0.11	2.31
Seawater	-0.27	0.13	2.78

[a] The added amount of carbonate into the tap and drinking water samples was accepted as true value, and the results of potentiometric titrimetry for sparkling water, baking powder and seawater samples were accepted as true value for the related samples.

[b] At first, F-test was applied in order to decide on the variance type, then the student's t-test was applied for equal or different variances accordingly.