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Analysis of carbonate and hydrogen carbonate in seawater and brines

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ABSTRACT

The practice common in desalination plants of determining carbonate by titration of a sample of water with acid to pH 8.3 or 8.1, and total alkalinity by titration to pH 4.5, leads to an underestimation of the amount of carbonate present in high ionic-strength samples, which in turn may lead to erroneous assessments of scaling potential. Well-established empirical equations for the dissociation constants of carbonic acid in seawater as a function of salinity and temperature were used to estimate the proportion of each carbonate species present in samples of Arabian Gulf seawater, desalination concentrate, and nanofiltration reject. Samples were then titrated and inflection points identified associated with the protonation of the carbonate ion and the protonation of the hydrogen carbonate ion. Colorimetric titration gave end-points consistent with these inflection points and with the equations of Millero et al. Standard test method ASTM D3875-15 gives values of close to zero for the carbonate concentration in samples which were found to contain up to 40% of their inorganic carbon as carbonate according to the other methods of estimation. Thus ASTM D3875-15 is not suitable for seawater or desalination brines.

Keywords: Brine; Carbonate; Alkalinity

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1. Introduction

Determination of the concentration of carbonate and hydrogen carbonate (bicarbonate) ions in seawater and in seawater desalination plant brines is of significant practical importance in desalination plant operations [1]. The carbonate concentration in desalination brines is an important determinant of the formation of the inorganic alkaline scales, $CaCO_3$ and $Mg(OH)_2$, and prevention of these scales is critical for maintaining efficient production of water in both membrane and thermal desalination processes. Knowledge of the ratio of carbonate and hydrogen carbonate in desalination brine is necessary for determining its buffer capacity, which is relevant for the mixing of brine both with seawater and other effluent streams in order to minimize environmental impacts of brine discharge.

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Pedagogically, a simple method of assessing carbonate and hydrogen carbonate ion concentrations in seawater is attractive in any chemical education environment with access to the sea. The carbonate/hydrogen carbonate buffer system is of great interest to humanity and is key to the topical discussion of 'ocean de-alkalinization'. Educators at the secondary or tertiary level may be tempted to use published standard methods, such as ASTM D3875-15, to introduce students to these measurements [2].

Measurement of the total alkalinity of seawaters or brines, as for freshwaters and process waters, is a straightforward titration with a clearly-defined end-point where pH changes rapidly with small changes in the amount of acid addition. pH = 4.3 or 4.5 is usually taken as the end-point for automatic titration to determine M-alkalinity (where 'M' is for 'methyl orange'; also referred to as 'T', for 'total'), which is conventionally expressed by water analysts in terms of calcium carbonate equivalents[1]. As the pK_a of the reaction $HCO_3^- + H^+ \rightarrow H_2CO_3$ (K_{a1}) becomes smaller with ionic strength, this method may lead to an underestimation of the alkalinity of seawater and brines.

To determine carbonate, most methods appropriate for freshwaters and process waters titrate to pH = 8.3, giving the P-alkalinity (where 'P' is for 'phenolphthalein'). The procedure recommended by ASTM International for brackish water, seawater, and brines is to titrate to pH = 8.1 [3]. Because the pK_a of the reaction $CO_3^{2-} + H^+ \rightarrow HCO_3^-$ (K_{a2}) reduces significantly with increasing ionic strength [4], application of methods based on the 'M' and 'P' endpoints defined by pH readings may lead to underestimation of the amount of carbonate in seawater and brines. For example, see the ocean acidification investigation of Buth [2], where P-alkalinity gives carbonate 'below limits of detection' for seawater). The dependence of pK_a values on ionic strength is very well known by physical oceanographers who do not make use of such approximations [5]. Note that for accuracy such researchers also take into account the contribution of other species present in seawater, such as the borate ion [6].

The common neglect of the variation of pK_a with ionic strength will have practical consequences in scale control and brine management and will lead to very erroneous conclusions regarding the buffer capacity of seawater. This use of pK_a values obtained in water of low total dissolved solids (TDS) also makes the very extensive data sets collected by desalination plant operators unsuitable for use in studying carbonate speciation in seawater.

Fig. 1 shows the carbonate speciation at salinities of 0, 35,000 and 50,000 ppm at 25°C fitted using relationships determined by Millero et al. [4] for salinities up to 500,000 ppm.

At a salinity of zero and $T = 25°C$, pK_{a2} is about 10.3, and at a pH of 8.1, a ratio of about 218:1 $HCO_3^-:CO_3^{2-}$ is expected. The pH required to maintain this ratio as salinity increases are shown in Fig. 2a. Similarly, at a salinity of zero and $T = 25°C$, at a pH of 4.5 a ratio of about 91:1 $H_2CO_3:HCO_3^-$ is expected. The pH required to maintain this ratio is shown in Fig. 2b. It is clear that standard methods, such as ASTM D3875-15, will provide erroneous conclusions about the chemistry of seawater in these applications and more care needs to be taken during analyses.

In this brief note, we have generated curves of pH as a function of amount of acid added for seawater and brines which would be assigned a very low or zero carbonates concentration by the ASTM Method D3875-15 [3]. We have identified the inflection points associated with the reactions $H^+ + CO_3^{2-} \rightarrow HCO_3^-$ and $H^+ + HCO_3^- \rightarrow H_2CO_3$ and determined that the amount of carbonate estimated from these curves is consistent with the equations of Millero et al. [4]. For a number of studies, the colorimetric endpoints were also determined and compared with the numerical pH values.

2. Materials and methods

0.1 N HCl (Takween, Sedres Chemical Solutions, Jubail, KSA) was used with a 50 mL Class 4 Titrette and pH monitored with a METTLER TOLEDO Seven CompactDuo pH probe with five-point calibration (pH = 2.00, 4.00, 7.00, 9.11, 11.00). Phenolphthalein indicator (BDH Indicators, Poole, England) was prepared by dissolving 0.5 g of phenolphthalein in 50 mL of absolute ethanol (BDH AnalaR, Poole, England) and diluting to 100 mL demineralized water. Methyl orange indicator was prepared by dissolving 0.05 g of methyl orange (BDH Indicators, Poole, England) in 100 mL demineralized water. Four to five drops of each indicator solution were added to each aliquot of water titrated.

Seawater was obtained from the Arabian Gulf. Samples were taken from the Ras Al-Khair Reverse Osmosis (RO) plant (27° 32′ N, 49° 9′ E) after initial filtration through a dual media sand/anthracite bed, with a total dissolved solids content of 47,700 ppm and initial pH of 7.73, and from the intake at the Al Jubail combined water and power plant (26° 54′ N, 49° 47′ E) with a TDS of 43,900 ppm and initial pH of approximately 8.24. RO (TDS = 64,300, pH = 7.18) and Multi-Stage Flash (MSF) brine (TDS = 63,900, pH = 8.87) were obtained from the Al Jubail Plants. The relative proportion of ionic species in these brines, with the exception of carbonate and hydrogen carbonate, should not differ from that of the Arabian Gulf seawater as routinely measured at SWCC plants by Inductively Coupled Plasma Optical Emission Spectrometry (for cations) and Ion Chromatography (for anions) (Table 1). One sample of nanofiltration brine obtained from a pilot-scale facility at the Al Jubail Plant was also analyzed (TDS = 84,700 ppm, pH = 7.86).

3. Results

In an initial experiment, 50 mL of seawater from the Ras Al-Khair RO Plant was titrated with 0.10 N HCl at a laboratory temperature of 23°C (Fig. 3). Besides the inflection point for the determination of P-alkalinity at about pH = 4.5, there are indications of an inflection point at approximately pH = 7.5. Using these inflection points as a basis for estimation of the carbonate present in the

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[1] Thus, whether the reaction is $H^+ + OH^- \rightarrow H_2O$, $2H^+ + CO_3^{2-} \rightarrow H_2CO_3$, or $H^+ + HCO_3^- \rightarrow H_2CO_3$, the alkalinity is calculated based on the amount of $CaCO_3$ required to react with the amount of acid added.

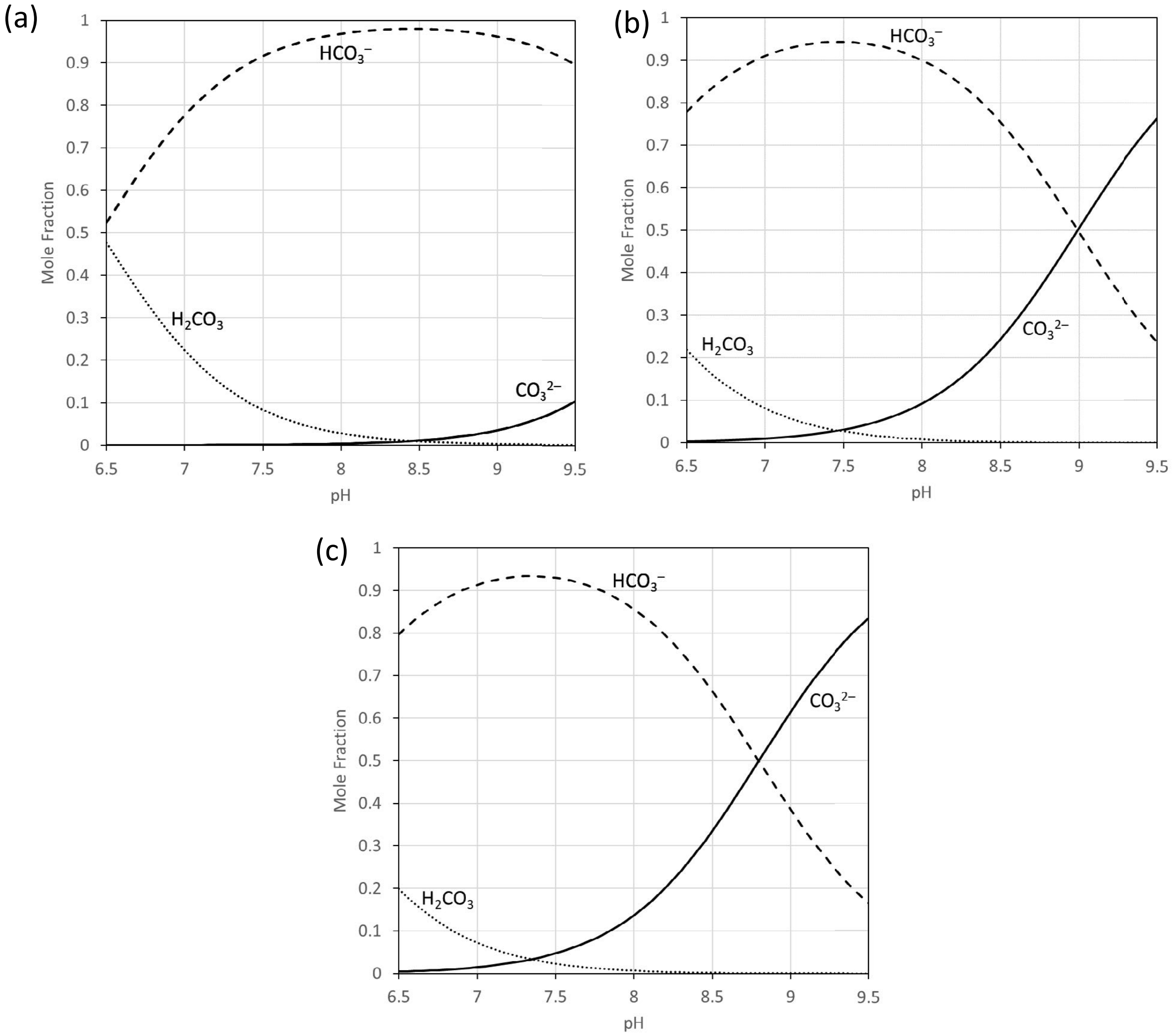

Fig. 1. Relative proportions of carbonate species at 25°C in the water of salinity (a) 0 ppm, (b) 35,000 ppm and (c) 50,000 ppm.

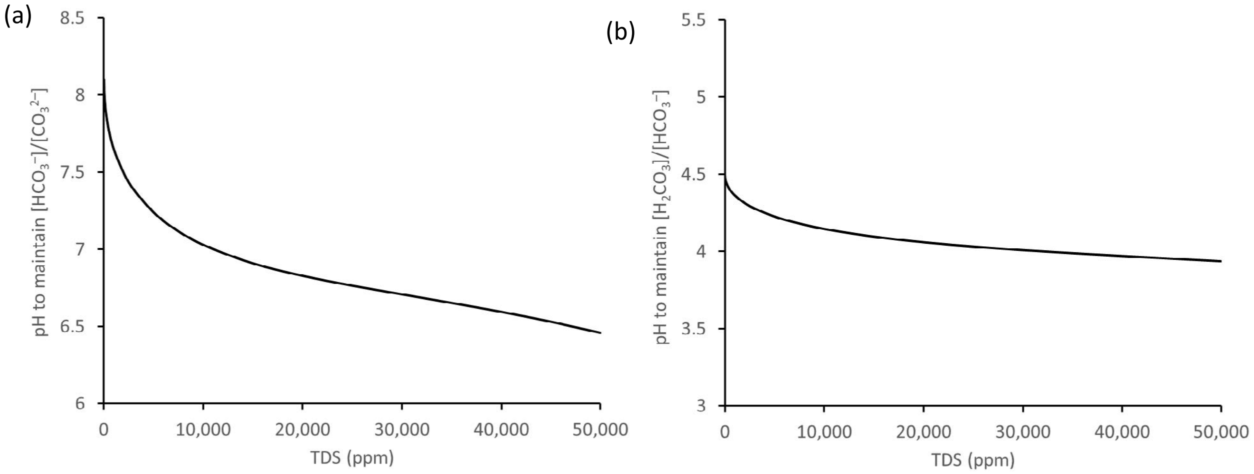

Fig. 2. pH values required to maintain a ratio of (a) 218:1 HCO_3^-:CO_3^{2-} and (b) 91:1 H_2CO_3:HCO_3^- at increasing TDS of solutions with the composition of seawater at 25°C, from the equations of Millero et al. [4].

sample gave 160 µm of CO_3^{2-} and 1.58 mM of HCO_3^-, for total alkalinity of 95 ppm $CaCO_3$ equivalents and an HCO_3^-/CO_3^{2-} the ratio of 9.9. This is approximately consistent with the model of Millero et al. [4], which suggests seawater at TDS = 47,700 ppm at pH = 7.73 and T = 25°C should have an HCO_3^-/CO_3^{2-} the ratio of 13.5.

In a second experiment, 100 mL samples of seawater from the intake at the Al Jubail combined water and power plant were titrated in triplicate with 0.10 N HCl at a laboratory temperature of 23°C (Table 2). Inflection points were determined by fitting a quadratic function to appropriate segments of numerical differentiation of the titration curve and taking the minimum point of these quadratic functions (Fig. 4).

All methods are in rough agreement on the total alkalinity of the seawater sample due to the relative insensitivity of the second inflection point to ionic strength and the rapid change in pH at this inflection point. However, the ratio of carbonate to hydrogen carbonate is significantly different from the three approaches. As the pK_a of the indicator species will vary with ionic strength in a parallel way to the pK_a of the carbonate and hydrogen carbonate ions, it is not surprising that the values obtained colorimetrically are in close agreement with the values predicted by the equation of Millero et al. [4]. While ASTM D375-15 systematically under-reports carbonate relative to the predicted value, carbonate appears to be over-reported by taking the inflection point on the titration curve as the end-point. This may be related to borate, which is reported to account for about 5% of seawater alkalinity [7] and with a pK_a of 8.60 at S = 35‰ and T = 25°C [8], is likely to be contributing to the first inflection point (i.e., the value obtained at this point will not be moles carbonate, but moles of carbonate + borate).

Investigations were next made of brines with a higher TDS, which in principle should have a higher proportion of

Table 1
Composition of Arabian Gulf seawater and nanofiltration brine

ppm	Arabian Gulf seawater	Nanofiltration brine
Total dissolved solids	44,500	84,700
Chloride (Cl^-)	23,500	48,300
Sodium (Na^+)	12,400	11,300
Sulfate (SO_4^{2-})	3290	21,000
Magnesium (Mg^{2+})	1,530	6,900
Calcium (Ca^{2+})	450	1,600
Potassium (K^+)	470	500

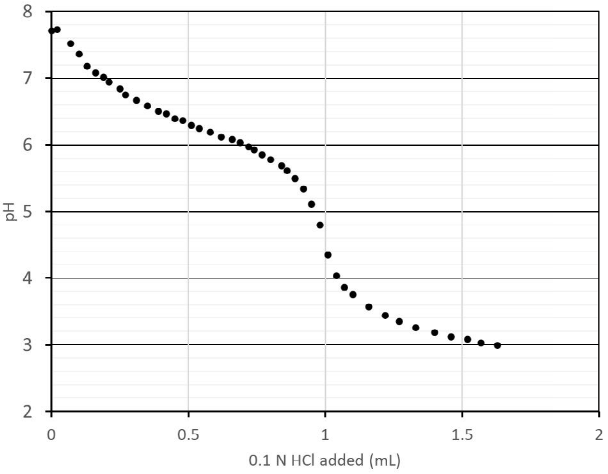

Fig. 3. Titration of filtered seawater from the Arabian Gulf (TDS = 47,700 ppm).

Table 2
Triplicate titration of unfiltered seawater from the Arabian Gulf (TDS = 43,900 ppm)

	# 1	# 2	# 3	Mean and Standard Deviation
Initial pH	8.21	8.24	8.26	8.24 ± 0.02
First inflection point pH	7.4	7.3	7.3	7.3 ± 0.1
Colorimetric P-alkalinity pH	7.50	7.53	7.52	7.52 ± 0.01
Second inflection point pH	4.5	4.3	4.5	4.4 ± 0.1
Colorimetric M-alkalinity pH	4.16	4.10	4.04	4.10 ± 0.05
[CO_3^{2-}] by inflection point (µm)	50	48	50	49 ± 1
[HCO_3^-] by inflection point (µm)	162	166	161	163 ± 2
[CO_3^{2-}] by colorimetry (µm)	44	41	42	42 ± 1
[HCO_3^- by colorimetry (µm)	184	193	189	189 ± 4
HCO_3^-:CO_3^{2-} by inflection point	3.3	3.5	3.2	3.3 ± 0.1
HCO_3^-:CO_3^{2-} by colorimetry	4.2	4.7	4.5	4.5 ± 0.2
HCO_3^-:CO_3^{2-} by equation of Millero et al. [4]	5.0	4.7	4.5	4.7 ± 0.2
HCO_3^-:CO_3^{2-} according to ASTM D375-15	22	22	17	20 ± 2
Total alkalinity by inflection points (ppm $CaCO_3$)	130	134	138	134 ± 3
Total alkalinity by colorimetry (ppm $CaCO_3$)	134	135	137	135 ± 1
Total alkalinity by ASTM D375-15 (ppm $CaCO_3$)	130	128	133	130 ± 2

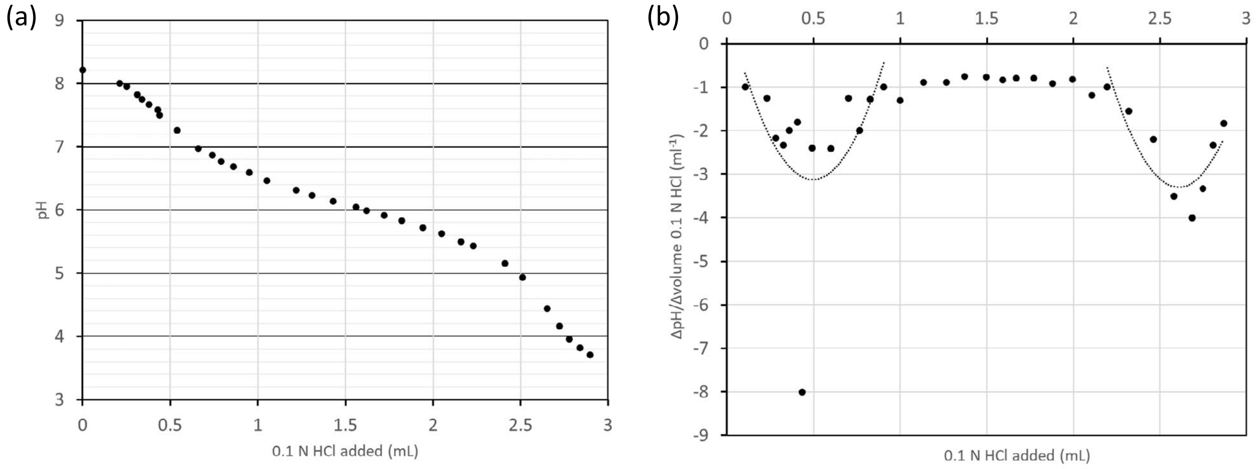

Fig. 4. Titration of seawater from Al Jubail Plant intake, initial pH = 8.21. (a) pH vs. acid added and (b) numerical derivative of titration curve (first quadratic: $16.013x^2 - 15.878x + 0.8132$; second quadratic $16.086x^2 - 3.889x + 106.07$) (other replicates in Fig. S1).

carbonate than seawater at the same pH and temperature (Table 3). An RO brine (100 mL aliquots, Fig. S2), MSF blowdown brine (100 mL aliquots, Fig. S3), and nanofiltration brine obtained from treatment at a pilot-scale facility from RO brine (50 mL aliquot, Fig. 5) were analyzed.

As for seawater, all three methods gave similar total alkalinities but very different ratios of carbonate to hydrogen carbonate ions. ASTM D375-15 gave values of this ratio most divergent from the values predicted from the equations of Millero et al. [4]. Colorimetric titration gave values most similar to the predicted values (despite the anomalously low pH for the M-alkalinity end-point for one of the MSF blowdown brine samples) while taking the inflection points in the titration curves again appeared to overestimate the contribution of the carbonate ion to alkalinity.

4. Discussion

A titration curve of coastal seawater (CRM Batch 30, TDS = 33,420 ppm) reported by Hernández-Ayón et al. [5] is similar to the seawater results shown in Fig. 6 and clearly shows two inflection points (Fig. 5). The relative positions of the two peaks are consistent with the predictions of the Millero et al. model [4], which predict a $HCO_3^-:CO_3^{2-}$ ratio of about 14 for seawater of pH = 7.85 at T = 25°C and TDS = 33,420 ppm.

Table 3
Titration of brines from Al Jubail Desalination Plants

Sample	RO brine		MSF blowdown brine		Nanofiltration brine
Total dissolved solids (ppm)	64,300		63,900		84,700
Initial pH	7.15	7.21	8.86	8.88	7.86
First inflection point pH	6.9	6.94	7.2	7.3	6.74
Colorimetric P-alkalinity pH	7.15	7.21	7.61	7.77	N/D
Second inflection point pH	4.2	4.37	4.1	4.5	3.6
Colorimetric M-alkalinity pH	4.29	4.08	4.22	3.83	N/D
[CO_3^{2-}] by inflection point (μm)	200	210	1,880	1,920	1,170
[HCO_3^-] by inflection point (μm)	210	203	480	300	940
[CO_3^{2-}] by colorimetry (μm)	0	0	1,660	1,640	N/D
[HCO_3^-] by colorimetry (μm)	2,450	2,520	780	1,080	N/D
$HCO_3^-:CO_3^{2-}$ by inflection point	10.4	9.7	0.26	0.14	0.81
$HCO_3^-:CO_3^{2-}$ by colorimetry	N/A	N/A	0.47	0.66	N/D
$HCO_3^-:CO_3^{2-}$ by equation of Millero et al. [4]	25.8	23.0	0.52	0.49	1.38
$HCO_3^-:CO_3^{2-}$ according to ASTM D375-15	0	0	1.22	1.05	0
Total alkalinity by inflection points (mg/L $CaCO_3$)	125	123	212	207	164
Total alkalinity by colorimetry (mg/L $CaCO_3$)	120	123	201	214	N/D
Total alkalinity by ASTM D375-15 (mg/L $CaCO_3$)	118	118	201	208	157

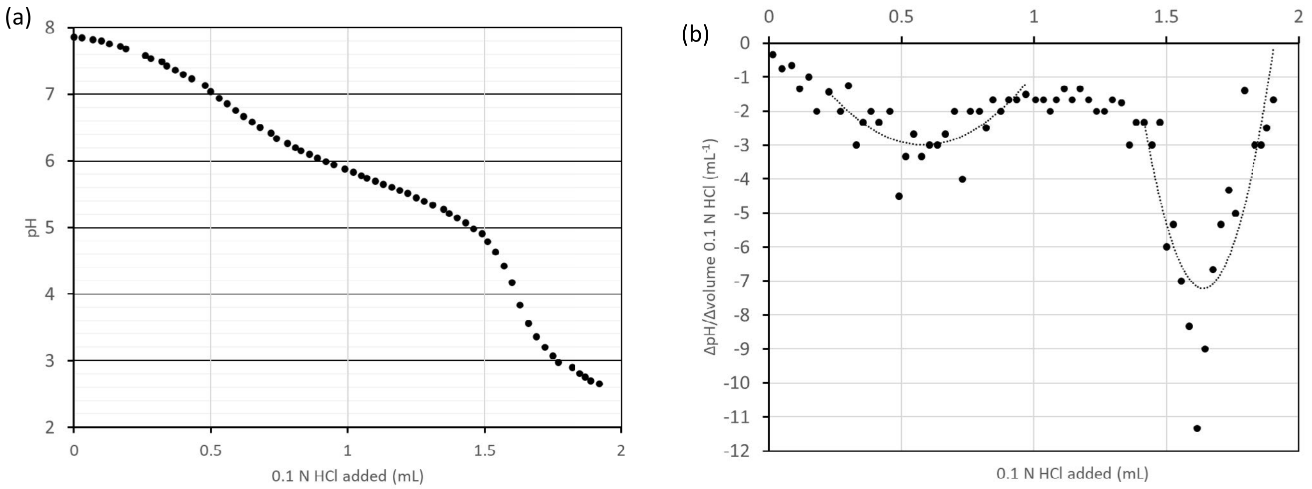

Fig. 5. Titration of nanofiltration brine. (a) pH vs. acid added and (b) numerical derivative of titration curve (first quadratic: $12.154x^2 - 14.19x + 1.1504$; second quadratic $98.831x^2 - 323.9x + 258.16$).

A titration curve of brine reported by Metrohm AG as an illustration of ASTM D3875-15 [9] (Fig. 7) also clearly shows a first inflection point, at a similar point in the curve as shown in the brine titration of Fig. 4. It is evident that the carbonate concentration of this brine is not 0 mg/L, as reported by ASTM D3875. It is also clear that the second inflection point is occurring well after pH = 4.5, so following the standard method for such a sample will lead to an underestimation of total alkalinity.

These examples should be sufficient to indicate that it is not appropriate to apply directly the titration methods for M and P-alkalinity developed for use in low TDS waters to seawaters, brines, or brackish waters with TDS above a few thousand ppm. Doing so will lead to a small underestimation in total alkalinity and is likely to significantly underestimate the contribution of the carbonate anion to total alkalinity. These examples also attest to the widespread use in the desalination community of these inappropriate methods.

It appears that colorimetric titration, as per the original definition of P and M-alkalinity, gives good agreement with the pK_a formulae of Millero et al. [4] and is appropriate for determining carbonate and hydrogen carbonate in seawater and typical brines. It also appears that determining the first inflection point of titration curves is not appropriate for determining carbonate, but systematically overestimates the contribution of carbonate to alkalinity. A contributing factor to this is almost certainly the contribution of borate, which has a similar pK_a to carbonate in seawater. A better estimate, where instrumentation such as an autotitrator is available (Fig. 6 and 7), would probably be afforded by taking the first maximum in the second derivative of the titration curve, rather than the first minimum in the first derivative of the titration curve.

Where a simpler method than colorimetric titration for routine analysis of carbonate is required, it is recommended that titrations similar to the ones illustrated here be carried out at and appropriate endpoints be identified corresponding to K_{a1} and K_{a2}. As a first approximation for seawater, a rule of thumb would be to use pH = 7.5, rather than 8.3 or 8.1, as the endpoint for the determination of carbonate.

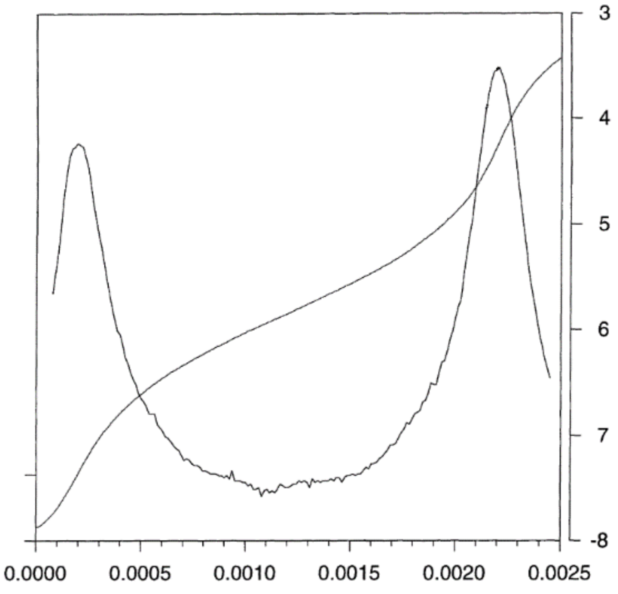

Fig. 6. Potentiometric titration of CRM batch 30 seawater. Reproduced by permission from Analytica Chimica Acta [5].

5. Conclusion

Colorimetric titration, as per the original definition of P and M alkalinity, gives accurate results of carbonate and hydrogen carbonate in seawater and brines up to the limits of the application of the rigorous formulae of Millero et al. [4]. However, adaptations of the original P and M alkalinity method which rely on titration to set pH values can give erroneous results when applied to seawater or brines if the pH values appropriate to low TDS waters are used. This includes the standard test

Sample	HCO_3^- / mg/L	CO_3^{2-} / mg/L
Brine	743	0

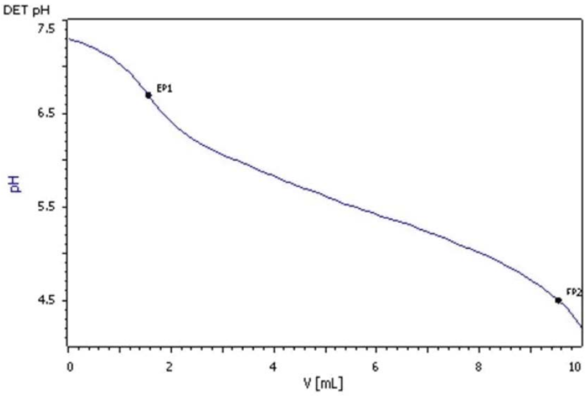

Fig. 7. Titration of brine according to ASTM D3875. Reproduced by permission of Metrohm AG [9].

method ASTM D3875-15, which should therefore not be used for determination of carbonate in seawater and brines.

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Supplementary information

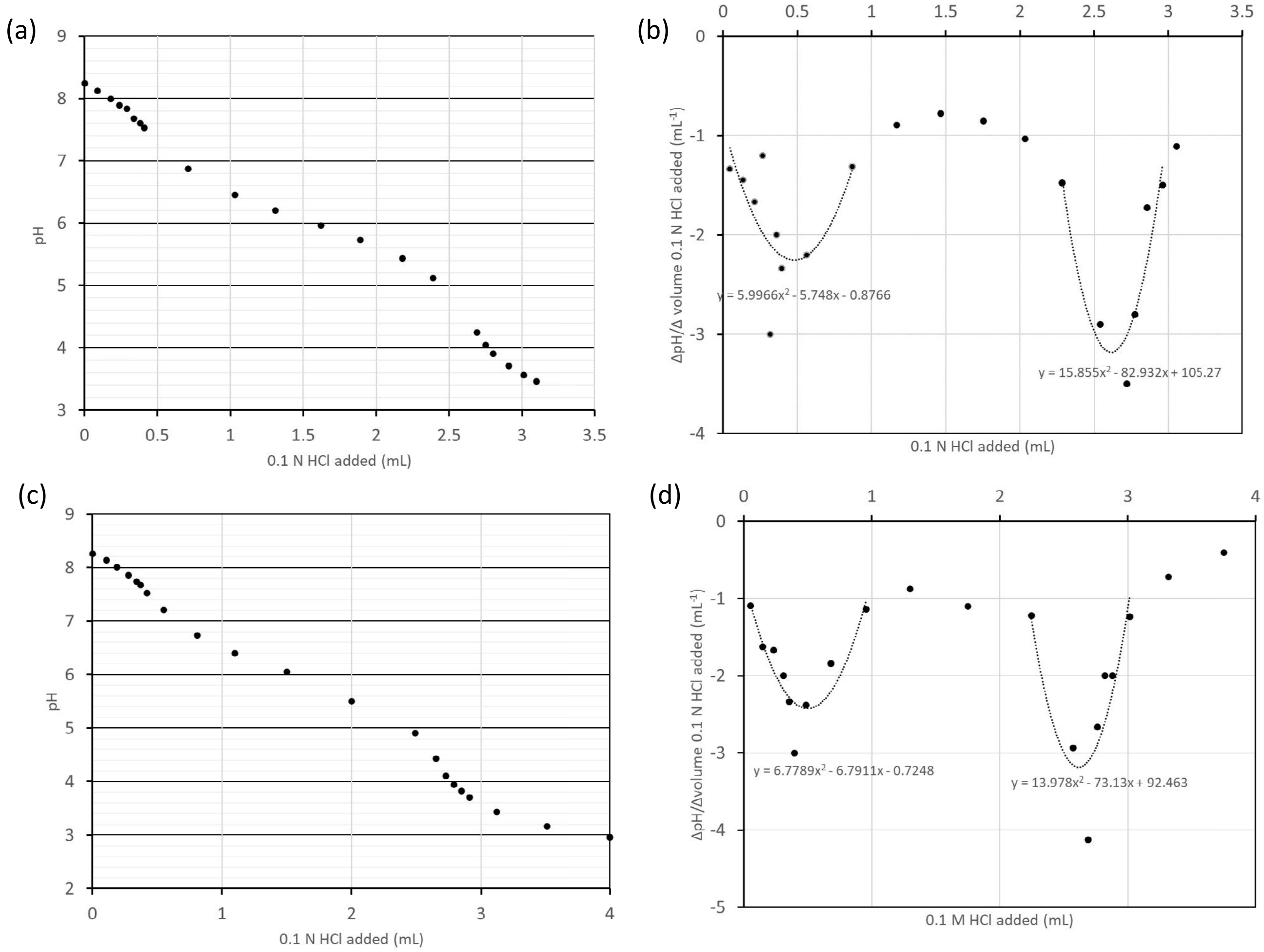

Fig. S1. Replicate determinations of alkalinity in unfiltered seawater samples from Arabian Gulf (TDS = 43,900 ppm). (a,b) initial pH = 8.24 and (c,d) initial pH = 8.26.

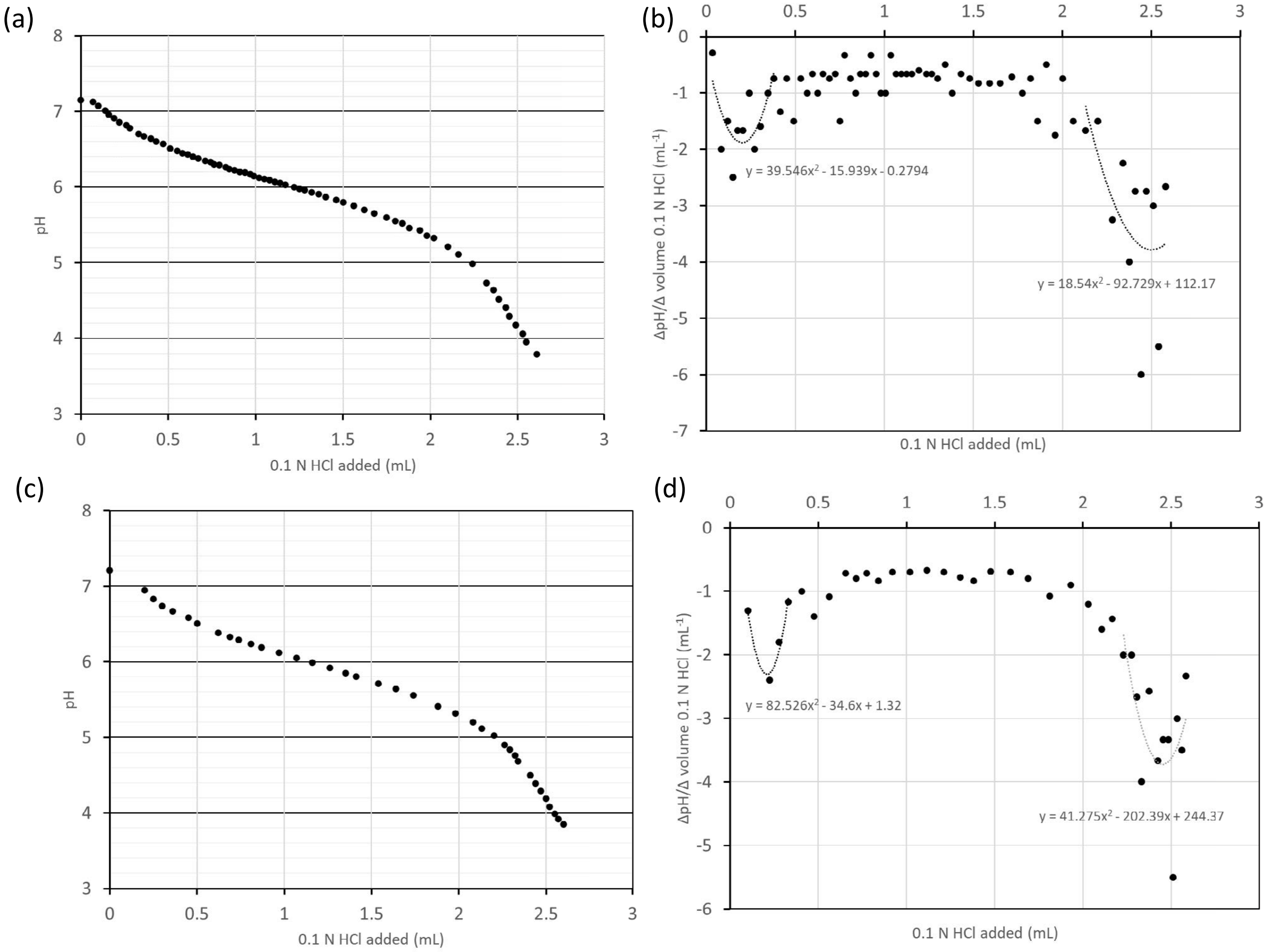

Fig. S2. Replicate determinations of alkalinity RO brine samples from Al Jubail Desalination Plant, Arabian Gulf (TDS = 64,300 ppm). (a,b) initial pH = 7.15 and (c,d) initial pH = 7.21.

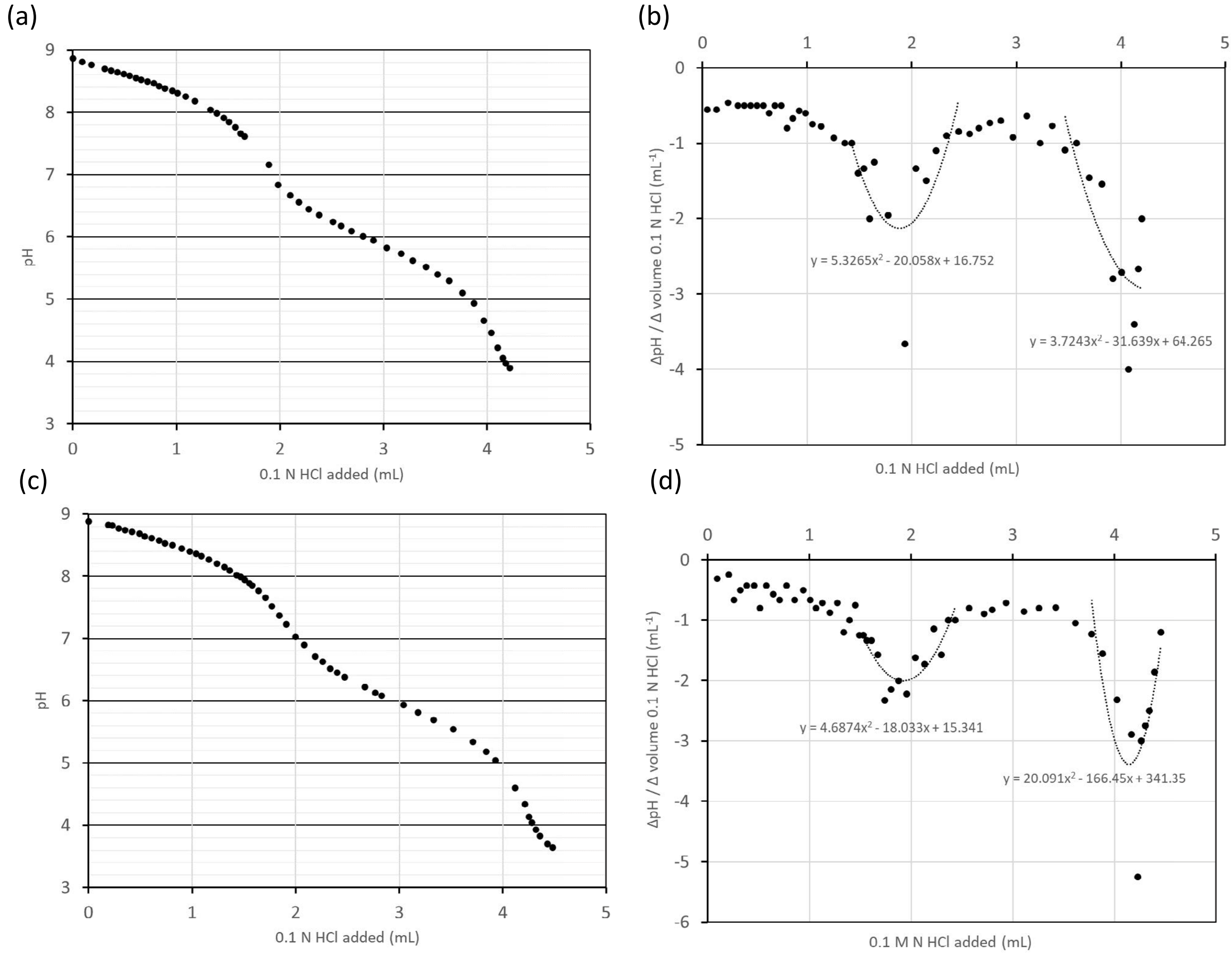

Fig. S3. Replicate determinations of alkalinity RO brine samples from Al Jubail Desalination Plant, Arabian Gulf (TDS = 63,900 ppm). (a,b) initial pH = 8.86 and (c,d) initial pH = 8.88.