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Esra Marvin

pH Measurement in High Ionic Strength Brines

Calibration of a combined glass electrode to obtain accurate pH measurements for use in a coupled single pass SWRO boron removal model

Abstract

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The purpose of this thesis was to calibrate a combined glass electrode to obtain accurate pH measurements in high ionic strength brines. pH measurements in high ionic strength brines are susceptible to significant errors when measured with standard calibrated electrodes. The work done in this thesis was part of a larger project carried out at the Israel Institute of Technology, where a new single pass boron removal process is being developed and modeled. The goal for the calibration was to obtain consistent and accurate pH measurements to the Pitzer-model. pH measurements with the new calibration can be used as input in a coupled single pass boron removal model and are expected to increase the accuracy of the boron removal model.

Three sets of experiments were carried out to achieve the goals and test the Pitzer model's ability to predict pH of high ionic strength solutions. The pH of borax and carbonate samples with varying amounts of synthetic seawater were measured with a Metrohm combined glass electrode. The measured pH values were compared to modelled values in PHREEQC-software. Several calibrations with varying amounts of NaCl added to standard buffers were also tested and compared to modelled values. The results showed that the difference between Pitzer modelled pH values and pH values measured with a standard calibrated electrode can be up to 0.1 pH unit, when measuring high ionic strength brines. The differences between other models and measured pH values were even larger. Adding NaCl to standard calibration buffers improved the pH measurement accuracy to the Pitzer model. A calibration with 0.75M NaCl added to standard phthalate, phosphate and carbonate buffers yielded accurate pH measurements of high ionic strength samples (up to 2.5 times the concentration of seawater). The accuracy reached was 0.03 pH unit to the Pitzer model.

Accurate and consistent pH measurements to the Pitzer model can be obtained by a simple and practical calibration procedure. Nevertheless, further work would be needed before wide scale use of the procedure. Also limiting wide scale application are the experimental parameters used in the Pitzer model. These experimental parameters do not have completely defined uncertainties; hence, a complete uncertainty statement for calibration standards and pH measurements cannot be given for the calibration tested in this thesis work.

Keywords	pH measurement, calibration, Pitzer model, seawater, brine, boron, boron removal, pH standard buffer, NIST, SIT, Minteq4

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Tämän opinnäytetyön tarkoituksen oli kalibroida yhdistelmä elektrodi, jotta korkean kokonaiskonsentraation omaavien suolaliuosten pH voitaisiin mitata tarkasti. pH mittaukset korkeissa kokonaiskonsentraation omaavissa suolaliuoksissa ovat alttiita virheille kun kalibroinissa käytetään standardi puskuriliuoksia. Tämän opinnäytetyön käytännön osuus oli osa suurempaa, Israel Institute of Technology:ssa tehtävää projektia. Projektissa kehitetään ja mallinetaan uutta käänteisosmoosiin perustuvaa boorin poisto menetelmää. Kehitettävän kalibroinnin tavoitteena oli saavuttaa pH mittauksia, jotka ovat yhdenmukaisia Pitzer-mallin kanssa. Uutta kalibrointia voidaan käyttää boorin poisto prosessin syöttöveden tarkempaan pH määritykseen. Tarkemman pH mittauksen arvoidaan parantavan prosessin mallinnusta.

Osana tätä opinnäytetyötä, laboratoriossa testattiin NaCl:n lisäystä puskuriliuoksiin ja Pitzer mallin yleistä kykyä mallintaa korkean kokonaiskonsentraation omaavia liuoksia. Borax ja karbonaatti näytteiden pH mitattiin standardi kalibroidulla elektrodilla ja uudella kalibroinnilla. Näytteisiin oli lisätty eri määriä synteettistä merivettä. Tuloksia verrattiin PHREEQC-ohjelmassa mallinnettuihin tuloksiin. Tulokset osoittivat, että standardi kalibroidun elektrodin ja Pitzer mallin ero voi olla jopa 0.1 pH yksikköä kun pH mittauksia tehdään korkean kokonaiskonsentraation omaavissa suolaliuoksisa. Muiden testattujen mallien ero oli vielä suurempi. pH mittausten tarkkuutta pystyttiin parantamaan lisäämällä NaCl:a kalibrointi liuoksiin. 0.75M NaCl konsentraatio kalibrointi liuoksissa parnasi pH mittausten tarkkuutta 0.03 pH yksiköön kun mitattavien näytteiden suolapitoisuus vastasi 2.5 kertaa merivettä.

Tässä opinnäytetyössä todennettiin, että Pitzer mallin kanssa yhdenmukaisia pH mittauksia voidaan saavuttaa yksinkertaisella ja käytännöllisellä kalibroinnilla. Kuitenkin lisää mittauksia ja tutkimusta tarvitaan ennekuin menetelmää voidaan alkaa käyttää laajemmin. Esteenä menetelmän laajemmalle käytölle on myös tällähetkellä Pitzer mallissa käytettävien parametrien epävarmuus. Pitzer mallin epävarmuustekijät vaikuttavat tässä työssä esitetyn kalibointri menetelmän ja pH mittausten epävarmuuteen, eikä täten kokonaista epävarmuus laskelmaa voida suorittaa.

Avainsanat	pH, pH-mittaus, kalibrointi, Pitzer-malli, merivesi, suolaliuos, boori, boorin poisto, pH standardi, puskuriliuos, NIST, SIT, Minteq 4

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The experience is one I will cherish for the rest of my life!

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Abbreviations

DIN	German Institute for Standardization
EMF	Electro motive force
EU	European Union
IUPAC	International Union of Pure and Applied Chemistry
LJP	Liquid junction potential
NIST	National Institute of Standards and Technology
RLJP	Residual liquid junction potential
SW	Seawater
SWRO	Seawater reverses osmosis
WHO	World Health Organization

1 Introduction

The purpose of this research and thesis was to develop a new pH calibration for a potentiometric pH measurement. The calibration should provide an accurate input for modelling of boron permeation in a single pass SWRO (seawater reverse osmosis) process.

The guideline for boron concentration in drinking water, given by the World Health Organization (WHO) is 2.4 mg/l [1] and 1 mg/l given by the European Union (EU) [2]. With current SWRO technologies typical boron values of 0.9-1.3 mg/l in permeate can be reached [3]. Although the EU and WHO guidelines can be reached with current technologies, many times large desalination plants are given even more stringent requirements for boron removal. Boron is naturally occurring in seawater and an essential micronutrient for plants [4]. But typical values for boron (0.9-1.3 mg/l) in SWRO permeate can be toxic to agricultural plants and render desalinated seawater useless for irrigation purposes [3]. For these reasons, there is likely to remain a future need for low boron concentration water to meet irrigation needs and legislative requirements [3].

Several methods for achieving low boron concentration water from SWRO exist. A new, more competitive single pass removal of boron utilizing low-energy SWRO membranes has been proposed by Nir et al. in their article: *"A novel approach for SWRO desalination plants operation, comprising single pass boron removal and reuse of CO_2 in the post treatment step"* [3]. The method involves acid dosage to the feed water, eliminating carbonate species and potential for fouling. Once the feed water pH is lowered, it can be cost efficiently raised back up to basic (pH >9). In this pH range the primary species of boron is the borate ion ($B(OH)_4^-$). The borate ion is well rejected by conventional membranes. In the work of Nir et al., boron concentration of 0.17 mg/l in permeates was reached using the described method.

pH is a common parameter measured in many fields of science and engineering including the medical, environmental and industrial fields. The use of pH as a measurement can be problematic due to the varying conventions and definitions of pH. An incomplete understanding and use of the definition and scales of pH can lead to significant inaccuracies in measurement applications where high precision and accuracy is needed.

In the work of Nir and Lahav, "Coupling mass transport and chemical equilibrium models for improving the prediction of SWRO permeate boron concentrations, Desalination (2012)" [5], it has been suggested that pH measurements calibrated according to the seawater scale could yield pH values of >0.1 pH units lower than those compared to values obtained with calibrated dilute standard buffers. In this case, errors from pH measurement caused by incorrect use of the pH scale could lead to significant errors in the modelling of boron removal. The removal of boron strongly depends on the pH of feed water. For accurate modeling of boron removal, a reliable and accurate pH measurement in high ionic strength brines is needed.

The main inconsistencies in pH measurements rise from the convention of assigning pH values to buffers. The assigned pH values for buffers are obtained using the Bates-Guggenheim convention and are only valid for dilute (<0.1 M) solutions [6, 11]. Also the assumption of liquid junction potentials to be constant when making measurements with electrodes containing a liquid junction can be a cause of significant error [6, 13]. However, a method based on the Pitzer virial equations, has been identified as having potential to be a more suitable model for high ionic strength solutions allowing assignment of pH to high ionic strength buffers. The Pitzer approach takes into account ion interactions in a solution and thus overcomes the limitations of the Bates-Guggenheim convention [7, 2177].

Thus, the goal of this thesis project was to achieve a pH calibration method for SW and higher ionic strength solutions yielding pH measurements consistent with the Pitzer based chemical equilibrium model that is used in modeling of brine processes.

Several methods for calibrating electrodes for use in SW exist but are relatively complicated and based on a different pH scale, the hydrogen ion concentration scale. The benefit of the calibration procedure presented in this thesis project is that it is more consistent with the conventional understanding and scale of pH. It also provides the possibility to calibrate for measurements in solutions exceeding the ionic strength of SW, which to the writers' knowledge has not been proposed or tested before.

2   pH Definition

One way of understanding pH is as an indirect measure of the strength of an acid or base. The Bronsted concept of acids and bases defines an acid as a substance that has the ability to donate a proton to a species. Bases are defined as the opposite of acids. A base is a substance that has the ability to accept protons from other species. With this concept of acids and bases, the strength of acids and bases are measured by the tendency for proton donation or acceptance. In aqueous solutions the strength of acids and bases are measured relative to the conjugate acid-base system of H_2O. The autoprotolysis or self-ionization of pure water is Kw 1.00×10^{-14} dm^2 mol^{-6} at 25ºC giving an exact pH of 7 for neutrality. An acid dissolved in H_2O will increase the concentration of H^+ yielding pH<7. A base dissolved in H_2O will increase the OH^- concentration yielding pH>7.

pH is related to the concentration of the hydrogen ion and the acid dissociation constant. The original definition of Sorensen 1909, see equation (1), relates pH to the negative logarithm of hydrogen ion concentration. This definition is only valid for infinitely dilute solutions [8, 98].

$$pH \; = \; -log\textbf{[H}^+\textbf{]} \tag{1}$$

In higher ionic strength solutions and other non-ideal solutions, ions can participate in short and long distance interactions reducing the reactivity of the ions compared to actual concentrations. This is called the effective concentration or the activity on an ion. In ideal and infinitely dilute solutions the activity coefficient of the ion tends towards 1. This results in no difference between concentration and activity. Any deviations from ideal behavior will decrease the effective concentration or reduce the activity. A more generic and recommended operational definition for pH is given by the International Union of Pure and Applied Chemistry (IUPAC) [7] and the National Institute of Standards and Technology (NIST) [6]. The IUPAC definition relates pH to the negative logarithm of the activity of the hydrogen ion see equation (2):

$$pH \; = \; -\textbf{log(}aH^+\textbf{)} \tag{2}$$

Even though pH defined by the activity of the hydrogen ion is more generic and a more accurate model for non ideal solutions, the definition still remains problematic. Activity

of a single ion is not a directly thermodynamically measurable quantity [6, 3]. This rais-
es the need for a convention and scale for the measurement of pH.

2.1 Operational pH Scale

A convention for pH measurement is needed due to the notational definition of pH and
inability to measure the activity of a single ion. The convention agrees upon a series of
standard solutions and the method for assigning pH values to them. Calibrating the pH
electrode with the standards allows for comparable pH measurements with a well de-
fined uncertainty. Two organizations maintaining and defining these standards are
NIST (United States) and the German Institute for Standardization (DIN).

2.2 pH measurement

The most common method for pH measurement is the potentiometric method. Various
other methods exist, but since the development of the hydrogen glass electrode, the
potentiometric method has become the most common method due to practicality. The
method gives good accuracy and is simple to use compared to other techniques. [6, 2]
Standards with a known pH are needed when measuring the pH of an unknown solu-
tion using electrodes with liquid junctions. This is because the liquid junction of the
electrode cannot be measured. The calculation of pH from the EMF of a cell with liquid
junction potential is given below by equation (3):

$$pH = -\log aH = \frac{E + (EpH + Ej)}{RT\, ln10/F}$$ (3) [6]

where E is the electromotive force (EMF) of the unknown solution, $RT\, ln\, 10\, /F$ the ideal
Nernstian response, EpH a constant for the electrode used depending on temperature
and pressure and Ej the liquid junction potential of the electrode. The term ($EpH+Ej$) is
not measurable for an electrode but can be assumed to be constant for a given system
[6, 2]. Assuming the term constant for a given electrode and similar measurement con-
ditions, the pH of an unknown solution can be calculated by making the measurement
first in a solution with known pH. The equation for calculating pH of an unknown using
a standard is given in equation (4), where (x) denotes the unknown solution and (s) the
standard solution:

$$pH(X) = pH(S) + \frac{Ex - Es}{RT\, ln10/F}$$ (4) [6]

If the standard differs significantly from the unknown solution, or if the Nernstian response is not ideal, two standards that bracket the unknown sample should be used [6, 2-3]. Equation (5) can then be used to calculate the pH of the unknown solution. In this equation, linearity is assumed between the two known standards:

$$pH(X) = pH(S1) + \frac{Ex - Es1}{Es2 - Es1} * [pH(S2) - pH(S1)]$$ (5) [6]

2.3 Assignment of pH to standard solutions

Several methods for assigning pH values to standard solutions are available and described by IUPAC and NIST. The methods are divided to primary and secondary methods based on the uncertainty of each method. Primary methods are completely understood and described yielding a low uncertainty [7, 2189]. Typically the primary method measures the pH of a standard without reference to any other standard as is done with the Harned Cell. Secondary methods have larger uncertainties related to them resulting from the use of cells with liquid junction potentials that cannot be fully described. Standard solutions are also divided to primary and secondary. Primary standard solutions are of the highest quality, and their pH value is assigned without reference to any other standard [7, 2190]. Secondary standards are of lower quality and values assigned to them are comparable to those of primary standards [7, 2190].

The assignment of pH to primary and secondary standards relies on the Debye-Hückel theory for obtaining the activity coefficient needed for calculating pH. The Debye-Hückel equation for activity coefficients, equation (6), has been experimentally proven to be a suitable estimate for electrolyte solutions up to 1M in ionic strength. [6, 5] In this equation, γ is the activity coefficient, A and B are constants, z is the ionic charge, I is the ionic strength, $å$ is the ionic size parameter, and b is an adjustable parameter:

$$\log \gamma_i = -Az_i^2 \sqrt{I} / (1 + Bå_i \sqrt{I}) + bI$$ (6) [6, 5]

By applying the Debye-Hückel equation for the activity coefficient the pH of a primary standard can be fully defined with a Harned cell. The Harned cell does not have a liquid junction thus, it does not require the use of any other standard when determining the pH. The ionic strength of NIST standards do not exceed 0.1M. At ionic strengths as low

as this, the last term in the Debye-Hückel equation and the ionic size parameter become insignificant. The Bates-Guggenheim convention utilizes this and recommends using 1.5 for terms *B* and *å* for solutions around 0.1M ionic strength. The Debye-Hückel equation is then reduced to equation (7): [6, 5]

$$\log \gamma_i = -Az_i^2\sqrt{I}/(1 + 1.5\sqrt{I}) \qquad \text{(7) [6, 5]}$$

The uncertainty in pH when using the Bates-Guggenheim convention is less than 0.005 pH unit. With this uncertainty the simplified Bates-Guggenheim convention can be used for the assignment of primary standards. [6, 5]

In addition to using a Harned cell, pH can also be assigned to a standard when the acid dissociation constant is known. The equation still involves the activity coefficients but in ratios, which reduces uncertainties related to knowing the exact value of them. [6, 3-4] An extension of the Henderson-Hasselbach equation is represented below in equation (8):

$$pH = pKa + log\frac{ma}{mHa} + log\frac{\gamma a}{\gamma Ha} \qquad \text{(8) [6, 4]}$$

Where *γ* are the activity coefficient and *m* are the molarities of the undissociated acid and its conjugate base.

2.4   Limitations of the pH scale

Even with the pH scale and conventions, pH measurements are not completely without problems. Electrodes with liquid junctions require standards and the assumption of a constant liquid junction potential (LJP) between the standard and test solution to be able to make accurate measurements. In reality the assumption is not true for many applications causing significant errors in pH measurements. Measurements made in samples of acid rain or biological fluids with a combined glass electrode have been reported to have significant errors up to 0.5 pH unit [6, 7]. Due to these large errors, the liquid junction should not be considered constant when measuring unknown samples.

The liquid junction is a junction between electrolytes of different composition [7, 2191]. In electrodes, it is a potential difference between the standard or sample and the filling solution. When sample and standard solutions differ significantly in composition, there

are errors in measurement caused by this difference [7, 2191]. This error is called the residual liquid junction potential (RLJP). The liquid junction is not a thermodynamically measurable variable. It cannot be fully defined, hence measurements made with an electrode with a LJP are considered secondary measurements by IUPAC and NIST. Secondary measurements have a larger uncertainty associated to them. Although the LJP is not measurable, it is known that it depends on variables such as temperature, concentration of salt bridge and filling solution, electrolytes used and the geometrical structure of the liquid junction [6, 7]. The LJP varies in time and periodical calibrations are needed to adjust the measurements.

The other problem with the pH scale rises from the use of the Bates-Guggenheim convention in assigning pH values to standards. The Bates-Guggenheim convention is valid only up to 0.1M ionic strength. Thus, there is currently no conventional way to assign pH to special calibration standards with higher ionic strength. The Debye-Hückel equation can be used up to 1M ionic strength, but the uncertainty of pH of the standard is increased to 0.02 pH unit. [6, 5-6] The more recent IUPAC paper form 2002, on pH measurement, identifies the Pitzer virial equation approach as a possible improvement over the Bates-Guggenheim convention for calculating activity coefficients. It is also suggested that some problems caused by LJP could also be overcome using the Pitzer approach. [7, 2177]

The Pitzer ion interaction model is an extension of the Debye-Hückel equation. It utilizes a virial equation approach where specific interactions for ions and solvents are taken into account in a linear combination of parameters. The Pitzer approach is a more realistic model allowing calculations of activity coefficients for ions in any ionic strength [9]. The Pitzer approach is generally accepted in the scientific community as it agrees well with experimental data and overcomes problems with high ionic strength solutions. Nevertheless, it should be noted that some discrepancies have been pointed out with non existing uncertainties for Pitzer parameters in literature. The available data of Pitzer parameters in literature are also still insufficient, restricting the use of it in certain applications [10].

3   Single-pass SWRO boron removal process

The new single pass boron removal process utilizes low energy SWRO membranes and CO_2 stripping to achieve a cost effective way to attain low boron concentration water. A process flow diagram of the process is presented below in Figure 1 [3].
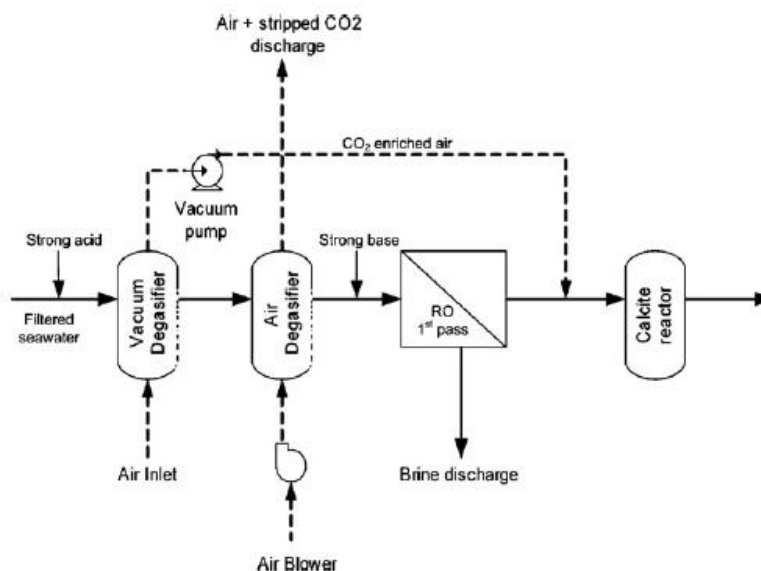
Figure 1. Process flow diagram of the single pass Boron removal process [3]

The process starts by lowering the feed water pH close to 4 with an addition of a strong acid. At this pH the main carbonate species is $CO_{2\ (aq)}$ Figure 2 [11]. The supersaturated CO_2 is then removed in two degasifying stages. The first stage removes 20-30% of CO_2 with a vacuum pump. The CO_2 removed in the first degasifying step is used later in the process to lower the pH and dissolve $CaCO_3$. The second degasifying step removes the rest of the CO_2, which is stripped to the atmosphere. The overall goal for CO_2 removal for the two degasifying steps is 96%. With most of the buffer capacity of the feed water eliminated, the feed water pH can be cost efficiently raised to 9 or slightly above. The aim of the pH raise is to drive the boric acid species to the borate ion which is well rejected by low energy SWRO membranes. While $CaCO_3$ scaling is avoided by removing inorganic carbon from the feed water by acid dosage, other scaling agents are avoided by keeping the raised pH within a narrow optimized range. The CO_2 removed in the first degasifying stage is finally introduced back in to the permeate of the SWRO membrane. The CO_2 lowers the permeate pH allowing $CaCO_{3(s)}$ to be dissolved at a reasonable rate in the final step of the process. [3, 276]
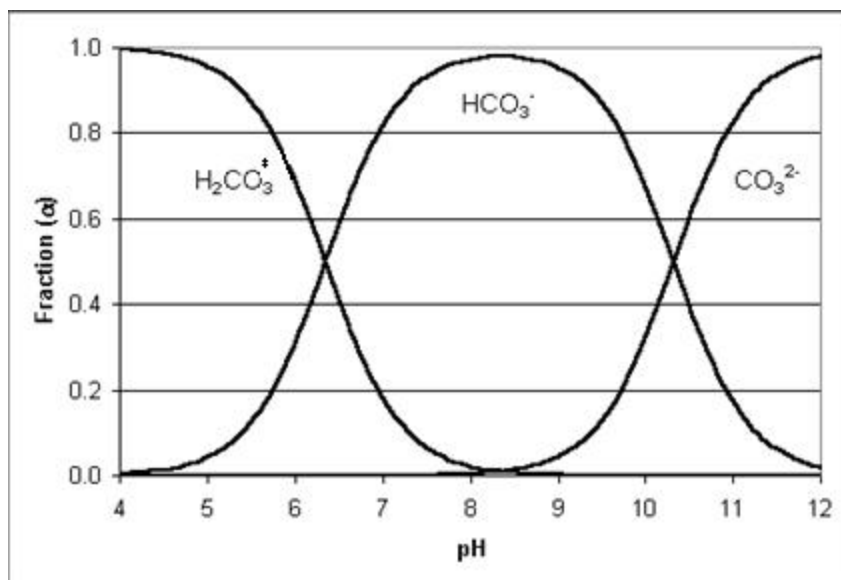
Figure 2. Carbonate system. $H_2CO_3^* = H_2CO_3 + CO_2(aq)$, only a small fraction (0.3%) appears as the acid H_2CO_3 [11]

4   Coupled Single Pass Boron Removal Model

Modelling is an important tool for process optimization and decision making. Having an accurate model for a designed process allows for testing the process in varying conditions and configurations. The results can be a valuable aid when making decisions for selecting the most-cost effective process and for operating the selected process.

The purpose of this chapter is to give a brief overview of a new modelling approach proposed by Nir and Lahav. The new approach describes a coupled model for improving prediction of boron permeate concentrations in a single pass boron removal SWRO membrane processes. Enough detail is given on the new approach to enable understanding of the process and to justify the experimental work done in this thesis project. Detailed descriptions of the models and numerical procedures used in the new approach are out of the scope of this work.

The new modelling approach combines traditional mass transfer models, the solution diffusion model and the polarization film layer model, with the Pitzer-based chemical equilibrium model in PHREEQC-software. The goal for the model was to be able to predict boron permeate concentrations with an uncertainty of 0.1 mg B /l. The 0.1 mg B /l in product water is a typical safety margin used in process design. [5]

To be able to accurately model boron concentrations in the product water, the model needs to consider all chemical processes affecting boron speciation. These include

changes in pH, temperature, salinity and recovery ratios [5, 2]. As mentioned earlier, pH is an important factor effecting boron speciation and hence boron removal in the SWRO process. Previous modelling approaches of membrane processes as described by Nir and Lahav, [5] have not been able to take into account the changing pH through the membrane. Typically, the earlier approaches have assumed constant pH through the membrane, although in reality, as it is well known, it changes through the membrane.

With the new coupled approach it is possible to model feed water changes and especially the pH changes through the membrane. This yields a more comprehensive model for boron removal in the membrane process. In practise, the membrane is divided into *n* sections. For each section, the mass transfer is calculated with the RO model. Output from the RO model is inserted to PHREEQC-software, which calculates new chemical equilibrium data for the input of the next section. In this way the complex changes and reactions in SW through the membrane are better considered. [5]

The results of experiments carried out in a pilot scale single pass SWRO process compared to modelled values for boron permeation with the new approach and earlier approaches show a clear improvement of modelling accuracy with the new approach [5, 4-5]. In the conclusions of Nir and Lahav, it is noted that further improvements of simulation predictions may be achieved by more accurate and consistent initial pH measurements [5, 6]. The initial pH measurements for comparing the two modelling approaches were obtained with a NIST standard calibrated electrode [5, 4]. This leads to the experimental work covered in this thesis, where a new calibration for a combined glass electrode was developed to better suit the needs of making pH measurements in high ionic strength solutions.

5   Experimental

In this thesis project, three sets of experiments were conducted. The goal of the experiments was to find a suitable pH calibration method for high ionic strength brines consistent with the Pitzer-based chemical equilibrium model. The first set of experiments aimed to quantify the difference between pH measurements made with a NIST standard calibrated electrode and pH values modeled with PHREEQC-software. In the second experimental set NaCl was added to NIST standard buffers to test if it would yield more precise pH measurements in high ionic strength brines. The objective was to find the ionic strength at which added NaCl would yield an accuracy of 0.03 pH unit to the

Pitzer model for measurements made in seawater and seawater brines. The final set of experiments was used to test the best NaCl calibration selected and the ability of the Pitzer model to predict acid-base reactions in seawater over the pH range from 4-10.

5.1 Materials

pH measurements were made using the Metrohm Aquatrode Plus (6.0257.600) combined glass electrode with an integrated Pt 1000 temperature sensor. The sensor was connected to the Metrohm 780 pH meter with pH, temperature and potential measuring modes. The resolutions for measurements with the 780 pH meter were 0.001 pH units, 0.1ºC and 0.1 mV.

Measurement conditions were kept constant at 25ºC with a MRC BL-30 circulating bath. In addition, laboratory temperature was kept as constant as possible with a thermostat set to 25ºC. Samples were stirred with a Metrohm 728 magnetic stirrer at constant speed.

The Metrohm 775 Dosimat automatic titration device was used to transfer HCl to samples in the final set of experiments. The automatic titrator had a better accuracy than standard volumetric burettes. Increased accuracy was needed when working at low buffer capacity of test solutions. A slight difference in HCl volume caused a significant difference in the pH of the solution.

Salts were weighed using an Ohaus Adventurer (AR2140) analytical balance with a resolution and standard deviation of 0.1 mg. Other equipment used in preparation of samples and standards included typical laboratory glassware and pipettes.

Synthetic seawater was prepared according to the recipe in Table 1. The recipe is a typical composition of SW with salinity 35. Other SW strengths were calculated by multiplying the molar ratios. $CaCl_2$ was not added to samples above 1xSW to avoid calcium precipitation. Synthetic SW was prepared on a volume basis as were all other solutions.

Deionized carbon free water was used in the preparation of SW stock solutions and all other calibration solutions, excluding phthalate, which is not sensitive to dissolved CO_2. Carbon free water was prepared by boiling deionized water for a minimum of 10 minutes.

Table 1. Preparation of 1kg synthetic seawater (1xSW = Salinity 35)

Salt	M g/mol	Ratio mol/Kg	0.1x SW [g]	0.5x SW [g]	1x SW [g]	1.5x SW [g]	2x SW [g]	2.5x SW [g]	3x SW [g]	4x SW [g]	5x SW [g]
NaCl	58.44	0.42764	2.499	12.496	24.991	37.487	49.983	62.478	74.974	99.965	124.96
Na2SO$_4$	142.04	0.02927	0.416	2.079	4.158	6.236	8.315	10.394	12.473	16.630	20.788
KCl	74.55	0.01058	0.079	0.394	0.789	1.183	1.578	1.972	2.366	3.155	3.944
MgCl$_2$+ 6H$_2$0	203.3	0.05474	1.113	5.564	11.129	16.693	22.257	27.822	33.386	44.515	55.642
CaCl$_2$ +2H$_2$0	147.02	0.01075	0.158	0.790	1.581	2.371	3.161	3.951	4.741	6.322	7.902

Certified Merck secondary standard buffers phthalate, phosphate, borax and carbonate were used for calibration of the Metrohm electrode in the first set of experiments. In later experiments phthalate and phosphate were prepared from Loba Chemie and Sigma-Aldrich analytical grade chemicals. Analytical grade (not certified) Merck sodium carbonate and Biolab-Chemicals sodium bicarbonate were used in the preparation of samples and calibration standards in the last set of experiments.

5.2   Experimental set 1

The pH of two buffers in seawater solutions ranging from 0.1xSW to 5xSW strength were measured and compared to three models in PHREEQC-software. The buffers used were NIST secondary buffers carbonate and borax. The models used in PHREEQC-software were SIT, Minteq 4 and Pitzer. Three replicates were conducted for each buffer at 8 different seawater strengths. The seawater strengths selected were 0, 0.1, 0.5, 1, 1.5, 2, 3, 4, and 5xSW. The Metrohm combined glass electrode was calibrated with NIST secondary standard buffers phthalate, phosphate and carbonate was used to make measurements. The calibration standards in this set of experiments were purchased from Merck.

0.01M borax and 0.025M carbonate solutions were prepared according to NIST and Merck instructions on a volume basis. Merck certificates for calibration buffers and NIST recipe used for preparation of borax can be found in Appendices 1 and 2. Salts needed to prepare 500 ml of synthetic seawater of different SW strengths were weighed. All salts were dried in 60-100ºC oven for a minimum of one hour and stored in a desiccator before weighing. Carbonate was dried in 250ºC for a minimum of two hours and stored in a desiccator over CaCl$_2$ according to Merck instructions.

Table 2.   Calculated cumulative addition of salts to 500 ml of sample solution

Salt	0.1xSW [g]	0.5xSW [g]	1xSW [g]	1.5xSW [g]	2xSW [g]	3xSW [g]	4xSW [g]	5xSW [g]
NaCl	1.2496	4.9983	6.2478	6.2478	6.2478	12.4956	12.4956	12.4956
Na_2SO_4	0.2079	0.8315	1.0394	1.0394	1.0394	2.0788	2.0788	2.0788
KCl	0.0394	0.1577	0.1972	0.1972	0.1972	0.3944	0.3944	0.3944
$MgCl_2 +6H_2O$	0.5564	2.2257	2.7822	2.7822	2.7822	5.5643	5.5643	5.5643
$CaCl_2 +2H_2O$	0.0790	0.3161	0.3951	0.3951	0.3951	0.7902	0.7902	0.7902

The weighed salts were added cumulatively to 500 ml of buffer and mixed with a magnetic stirrer for approximately 10 minutes or until all salts were dissolved. Calculated cumulative additions of salts are presented in Table 2. After each stepwise addition of salt and stabilization of solution to new SW strength, temperature, pH, and mV of the sample was recorded. Stirring speed was kept constant during recording of pH. First 2 runs of borax measurements were carried out in 25ºC room temperature. All Carbonate measurements and one set of borax measurements were conducted in a water bath kept at constant 25ºC. The circulating water bath system was assembled to keep solution temperature more stable during measurements.

5.3   Experimental set 2

The pH of 0.025M carbonate and 0.1M borax samples with varying amounts of synthetic seawater were measured with a Metrohm combined glass electrode. The electrode was calibrated with NIST secondary buffers: phthalate, phosphate and carbonate prepared with varying amounts of NaCl. Each sample was measured with 5 different calibrations. The molar amounts of NaCl used for the calibrations were 0M, 0.25M, 0.5M, 0.75M and 1M. pH values assigned to new calibrations were obtained by modelling the solutions in PHREEQC with the Pitzer model. Four replicate measurements were made with carbonate samples and three replicates with borax samples. Seawater strengths used for the samples were: 0, 0.5, 1, 1.5, 2 and 2.5 X SW. The last carbonate samples were prepared from a lower analytical grade carbonate to see if it could be used in future experiments.

Sample and calibration solutions were prepared from higher concentration stock solutions to reduce weighing errors. Correct amounts of stock solutions were pipetted to 100 ml volumetric flasks and filled to mark with decarbonized-deionized H_2O. Table 3 presents the stock solutions used and the amount pipetted to each calibration solution. Table 4 presents the preparation of samples from stock solutions. Calcium carbonate was not added to carbonate samples to avoid calcium carbonate precipitation.

Table 3.   Preparation of calibration standards from stock solutions

Calibration buffer 100 ml	0.2M Phtalate [ml]	0.1M Phos-phate [ml]	0.1M Car-bonate [ml]	4M NaCl [ml]
Phtalate/Phosphate/Carbonate	25	25	25	0
0.25M NaCl	25	25	25	6.25
0.5M NaCl	25	25	25	12.5
0.75M NaCl	25	25	25	18.75
1M NaCl	25	25	25	25

Table 4.   Preparation of samples from stock solutions

Sample 100 ml	Seawater x4 [ml]	0.1M Car-bonate [ml]	0.04M Bo-rax [ml]	1.075M CaCl2 [ml]
0.01MBorax+0xSW	0	-	25	0
0.01MBorax+0.5xSW	12.5	-	25	0.5
0.01M Borax+ 1xSW	25	-	25	1
0.01MBorax+1.5xSW	37.5	-	25	1.5
0.01M Borax+2xSW	50	-	25	2
0.01MBorax+2.5xSW	62.5	-	25	2.5
0.025MCarbonate+0xSW	0	25	-	-
0.025MCarbonate+0.5xSW	12.5	25	-	-
0.025MCarbonate+1xSW	25	25	-	-
0.025MCarbonate+1.5xSW	37.5	25	-	-
0.025MCarbonate+2xSW	50	25	-	-
0.025MCarbonate+2.5xSW	62.5	25	-	-

All pH measurements and calibrations were made in 25 ml beakers with a magnetic stirrer at constant mixing speed. Solution temperature was kept constant by conducting measurements in a 25ºC water bath. pH, temperature and mV readings were recorded for all samples. Calibration data for each different NaCl calibration was also recorded.

5.4   Experimental set 3

The ability of the Pitzer model to predict acid-base reactions in seawater was tested with sample solutions consisting of 0.0025M carbonate, 0.001M borax, synthetic sea-water ranging from 0 to 2.5xSW and HCl ranging from 0M to 0.01M. pH measurements were made with a Metrohm combined glass electrode. The electrode was calibrated with NIST secondary buffers phthalate, phosphate and carbonate prepared in a 0.75M NaCl solution. One replicate was made at 2xSW strength. In total 4 different SW strengths with 6 different HCl concentrations were used.

The 100 ml samples were prepared from 4xSW, 0.04M borax, 0.1M carbonate, 1.075M CaCl$_2$ and 0.1M HCl stock solutions. A quantity of 2.5 ml of borax and carbonate stock solution was pipetted to each sample. Correct amounts of SW and CaCl$_2$ stock were pipetted to obtain samples with 1, 1.5, 2 and 2.5 x SW strength. 0, 3, 5, 7, 9 and 10 ml of 0.1M HCl were added to appropriate samples with a Metrohm automatic pipette.

Table 5 clarifies the preparation of the samples. The 0.75M NaCl calibration buffers were prepared as in the second set of experiments (see Table 3).

pH measurements and calibrations were made in 25 ml beakers over a magnetic stirrer at constant mixing speed. Sample temperatures were allowed to stabilize to 25ºC in a water bath before recording pH, mV and temperature readings. Carbonate was pipetted to each sample immediately before measurement to reduce errors in pH readings caused by atmospheric CO_2 interaction.

Table 5.   Preparation of acid-base samples from stock solutions

Sample	Seawater x4 [ml]	0.1M Carbonate [ml]	0.04M Borax [ml]	1.075M CaCl2 [ml]	0.1M HCl [ml]
SWx1+0HCl	25	2.5	2.5	1	0
SWx1+3HCl	25	2.5	2.5	1	3
SWx1+5HCl	25	2.5	2.5	1	5
SWx1+7HCl	25	2.5	2.5	1	7
SWx1+9HCl	25	2.5	2.5	1	9
SWx1+10HCl	25	2.5	2.5	1	10
SWx1.5+0HCl	37.5	2.5	2.5	0	0
SWx1.5+3HCl	37.5	2.5	2.5	0	3
SWx1.5+5HCl	37.5	2.5	2.5	1.5	5
SWx1.5+7HCl	37.5	2.5	2.5	1.5	7
SWx1.5+9HCl	37.5	2.5	2.5	1.5	9
SWx1.5+10HCl	37.5	2.5	2.5	1.5	10
SWx2+0HCl	50	2.5	2.5	0	0
SWx2+3HCl	50	2.5	2.5	0	3
SWx2+5HCl	50	2.5	2.5	2	5
SWx2+7HCl	50	2.5	2.5	2	7
SWx2+9HCl	50	2.5	2.5	2	9
SWx2+10HCl	50	2.5	2.5	2	10
SWx2.5+0HCl	62.5	2.5	2.5	0	0
SWx2.5+3HCl	62.5	2.5	2.5	0	3
SWx2.5+5HCl	62.5	2.5	2.5	2.5	5
SWx2.5+7HCl	62.5	2.5	2.5	2.5	7
SWx2.5+9HCl	62.5	2.5	2.5	2.5	9
SWx2.5+10HCl	62.5	2.5	2.5	2.5	10

$CaCl_2$ was not added to higher pH or low acid addition samples with SW strength >1 to avoid $CaCO_3$ precipitation. See table 5 above.

6 Results

6.1 Experiment set 1

The Pitzer approach has been experimentally shown to be consistent and in good agreement with pH values obtained with the conventional Bates-Guggenheim method [12, 13, 14]. The additional benefit of using the Pitzer approach is overcoming obstacles when measuring solutions with ionic strength exceeding the limits of B-G convention. This experiment was carried out to verify the Pitzer model as a more accurate model for high ionic strength solutions and to quantify the difference between the Pitzer model and measurements made in high ionic strength solutions with a standard calibrated electrode. NIST standard buffers borax and carbonate with varying compositions of synthetic SW were measured with a NIST calibrated electrode and compared to pH values modeled with PHREEQC-software. Modelled values were obtained with the Pitzer (Macinnes scaled), SIT and Minteq4 models.

Figures 3 and 4 show graphed values for three replicates of 0.1M borax and 0.025M carbonate buffer with cumulative additions of synthetic SW salts.
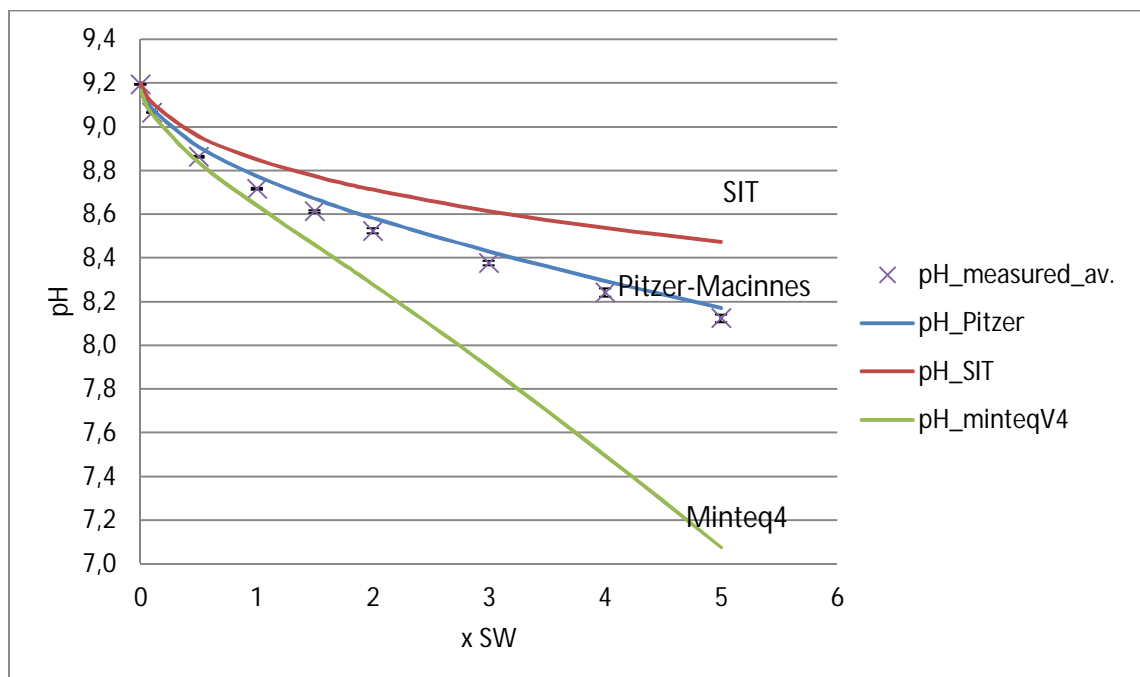
Figure 3. Modelled and measured average pH for borax with SW additions
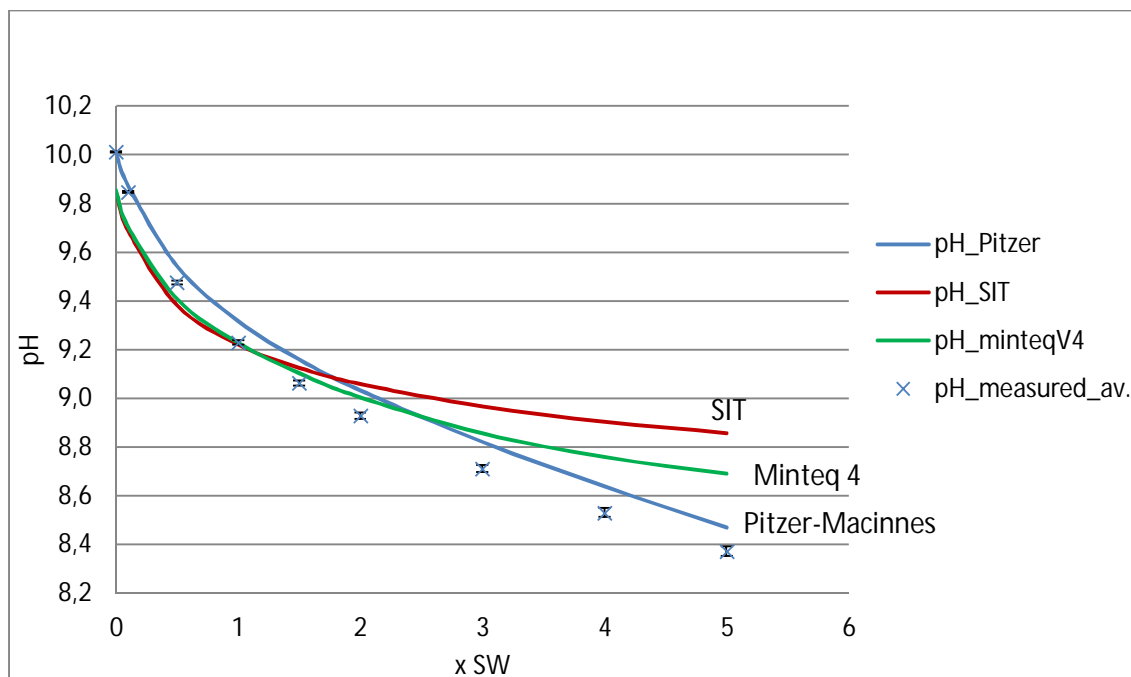
Figure 4. Modelled and average measured pH for carbonate with SW additions

From the graphs it is visible that the Pitzer model is the best model for the measured pH values. The ΔpH (modeled – measured pH) increases for the SIT and Minteq4 models as ionic strength of the solution increases. The ΔpH for the Pitzer model does not exceed 0.06 pH unit for borax and 0.11 pH unit for carbonate. The standard deviation varied between 0.002 and 0.019 for borax measurements and between 0.003 and 0.021 for carbonate measurements. For both carbonate and borax, the standard deviation increases with increasing ionic strength. The increase in standard deviation is likely caused by weighing errors which cumulate as salts are added to samples. The graphed data is also presented in Tables 8 and 9 in Appendix 3.

Temperature readings for the first two borax measurements varied slightly as no water bath was used. For carbonate measurements temperature readings were more stable. Sample temperature typically stabilized at about 25.3ºC as the result of taking into use the circulating water bath. For both carbonate and borax the pH decreases with increase in ionic strength. The pH decreases as the result of ionic interactions reducing the effective concentration. The same effect is cited and observed by Brown and Milton [15]

Regression was also carried out on measured and modeled data. See Figure 5 for borax and Figure 6 for carbonate.

Figure 5. Linear regression for borax samples
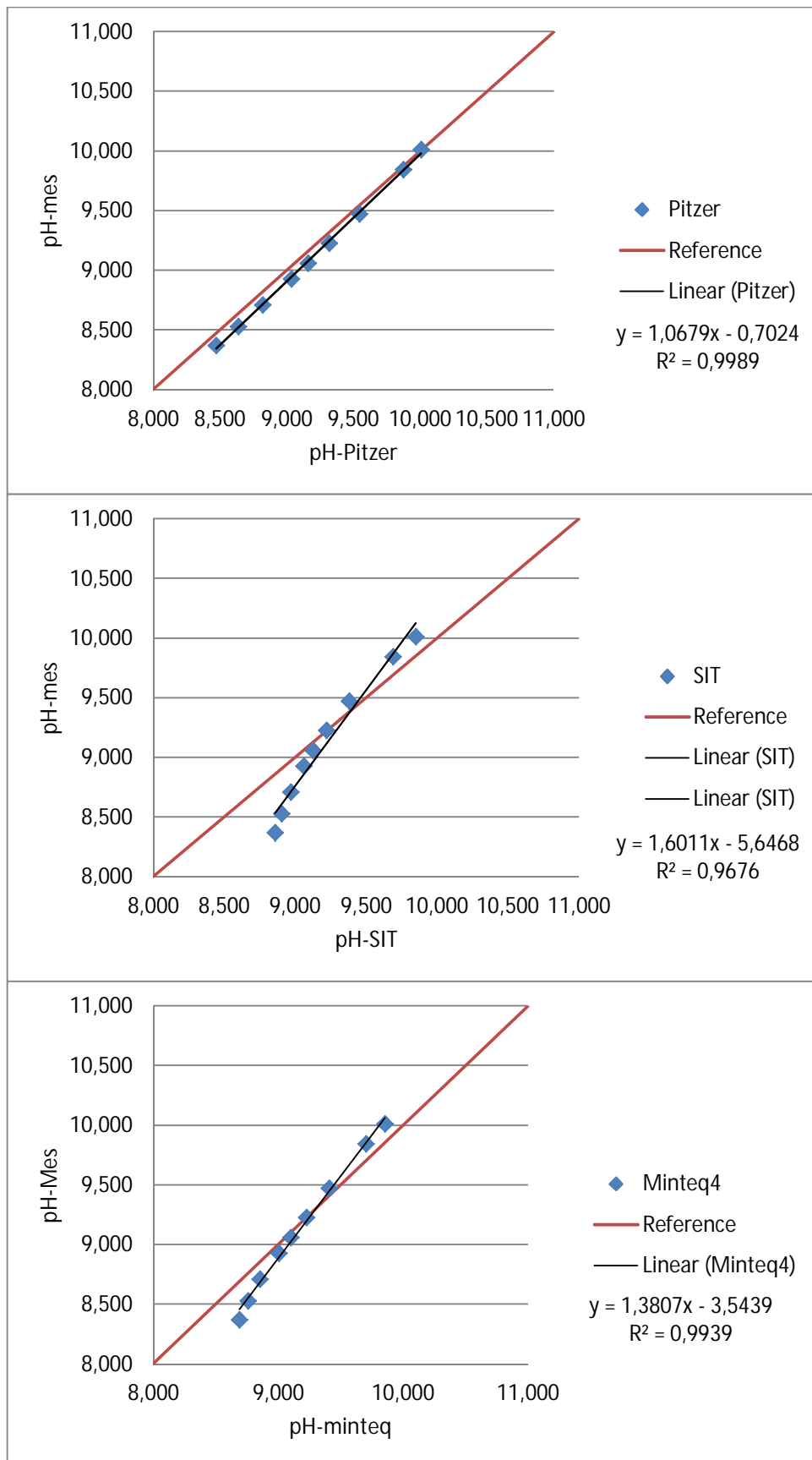
Figure 6. Linear regression for carbonate samples

The slope and intercept of the regression of each model was compared to the reference (ΔpH = 0). This shows how close the measured values are to the modeled. Large deviations from the reference slope 1 and intercept 0 indicate a larger difference between modeled and measured values. For both carbonate and borax the slop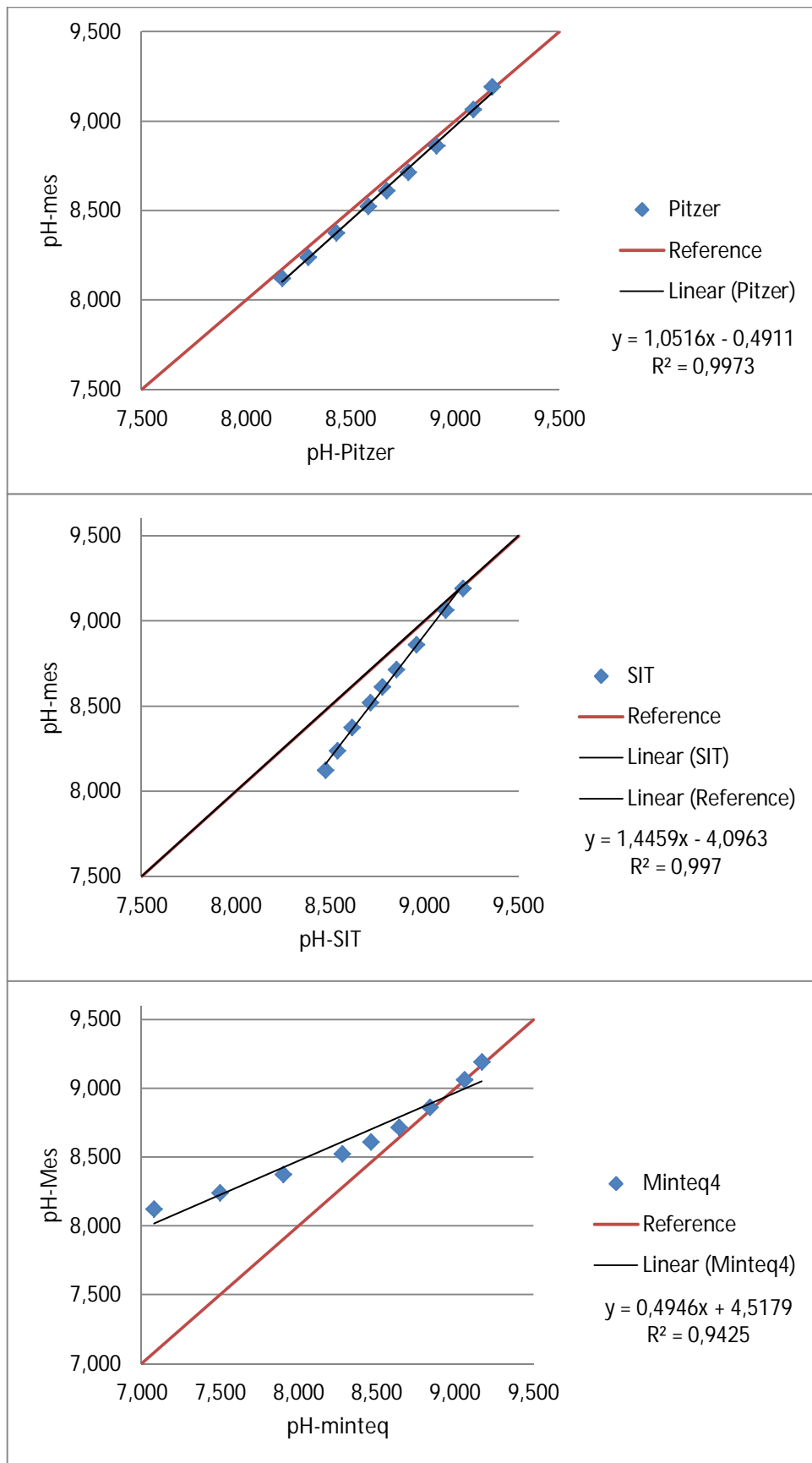e and intercept were closest to the reference indicating a good fit of measured values to the Pitzer model. Although the fit is good the 95%-confidence interval for the slopes and intercept indicate that there is a true systematic difference between measured and modeled values. The regression analysis output is presented in Appendix 4.

6.2   Experiment set 2

The Metrohm combined glass electrode was calibrated with NIST secondary standard buffers phthalate, phosphate and borax or carbonate prepared in varying concentrations of NaCl solution. The method was based on reducing the liquid junction potential by making calibrations in similar solutions to measurements. NaCl was selected and tested for calibration as it is the main component in SW and expected to have the largest effect on the effective concentration. The 0.025M carbonate and 0.1M borax samples in 0, 0.5, 1, 1.5, 2 and 2.5 XSW were measured with the different NaCl calibrations. Concentrations of 0, 0.5, 0.75 and 1M NaCl were selected. The Pitzer model in PHREEQC was used to model pH values assigned to calibration and sample solutions. The Modelled pH values for carbonate and borax in varying SW strength are presented in table 6.

Table 6.   Modeled Pitzer pH values for borax and carbonate in synthetic SW

Borax + SW Strength	Ionic Strength	pH borax
0	0.08	9.180
0.5	0.38	8.910
1	0.76	8.757
1.5	1.16	8.659
2	1.57	8.561
2.5	2.00	8.471
Carbonate + SW Strength	Ionic strength	pH carbonate
0	0.10	10.008
0.5	0.42	9.541
1	0.78	9.309
1.5	1.04	9.143
2	1.55	9.003
2.5	1.95	8.878

The desired accuracy for pH measurements was 0.03 pH unit, which is graphed as dotted lines. In Figures 7 and 8 the ΔpH of borax and carbonate is plotted against ionic

strength. From the data it can be seen that with the NIST standard calibration, Cal1 (no added NaCl), the differences between modeled and measured pH values are above the desired 0.03 pH unit accuracy for samples with SW (ionic strength >0.08). An Improvement in measurement accuracy can be seen for samples with high ionic strength when NaCl is used for calibration.
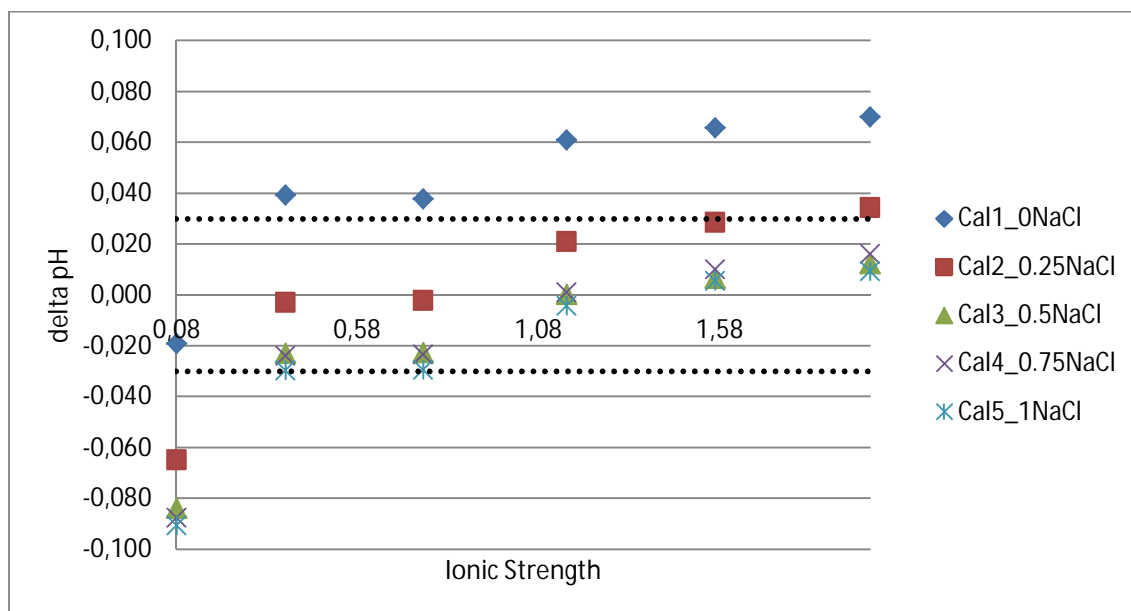
Figure 7. ∆pH of borax with different NaCl calibrations
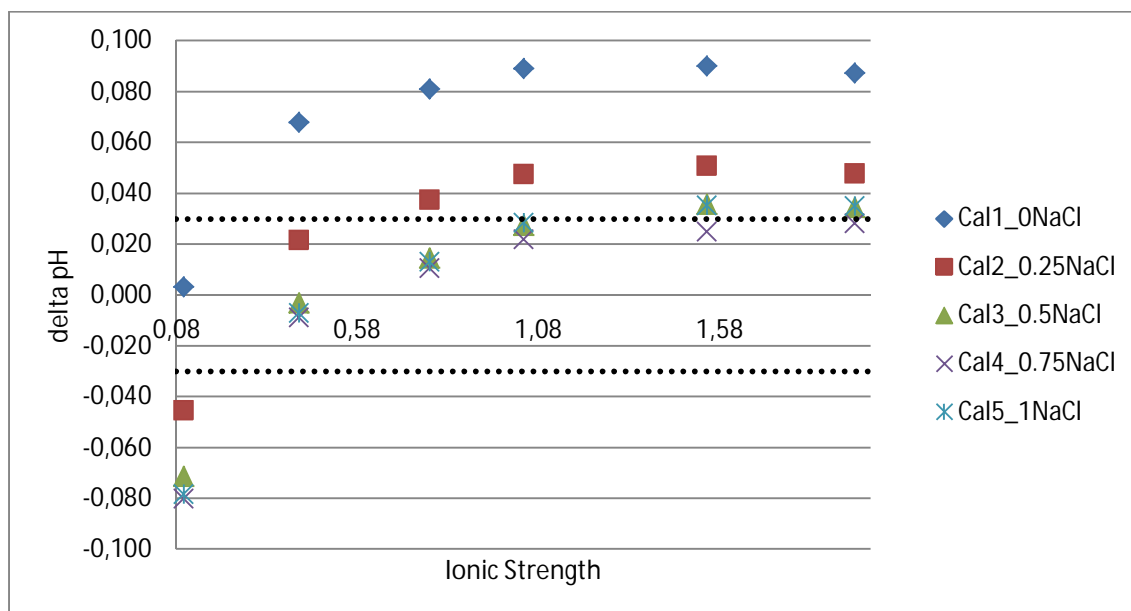
Figure 8. ∆pH of carbonate with different NaCl calibrations

From the plots it is visible that calibrations with 0.5M, 0.75M and 1M NaCl give acceptable results for the whole salinity range with borax and carbonate. Although, at lower ionic strengths (0.38 and 0.76) borax samples measured with the 1M NaCl cali-

bration yielded ΔpHs very close or exactly 0.03 pH unit. Carbonate with 0.5M and 1M NaCl calibrations yielded similarly less accurate results at higher ionic strengths (1.55 and 1.95). The accuracy was slightly lower than desired but still within one standard deviation away.

The calibrations were also compared to each other by calculating the area between the reference line and the calibration data. See Figure 9. The calibration with the smallest area or integral is the best calibration between the selected range.
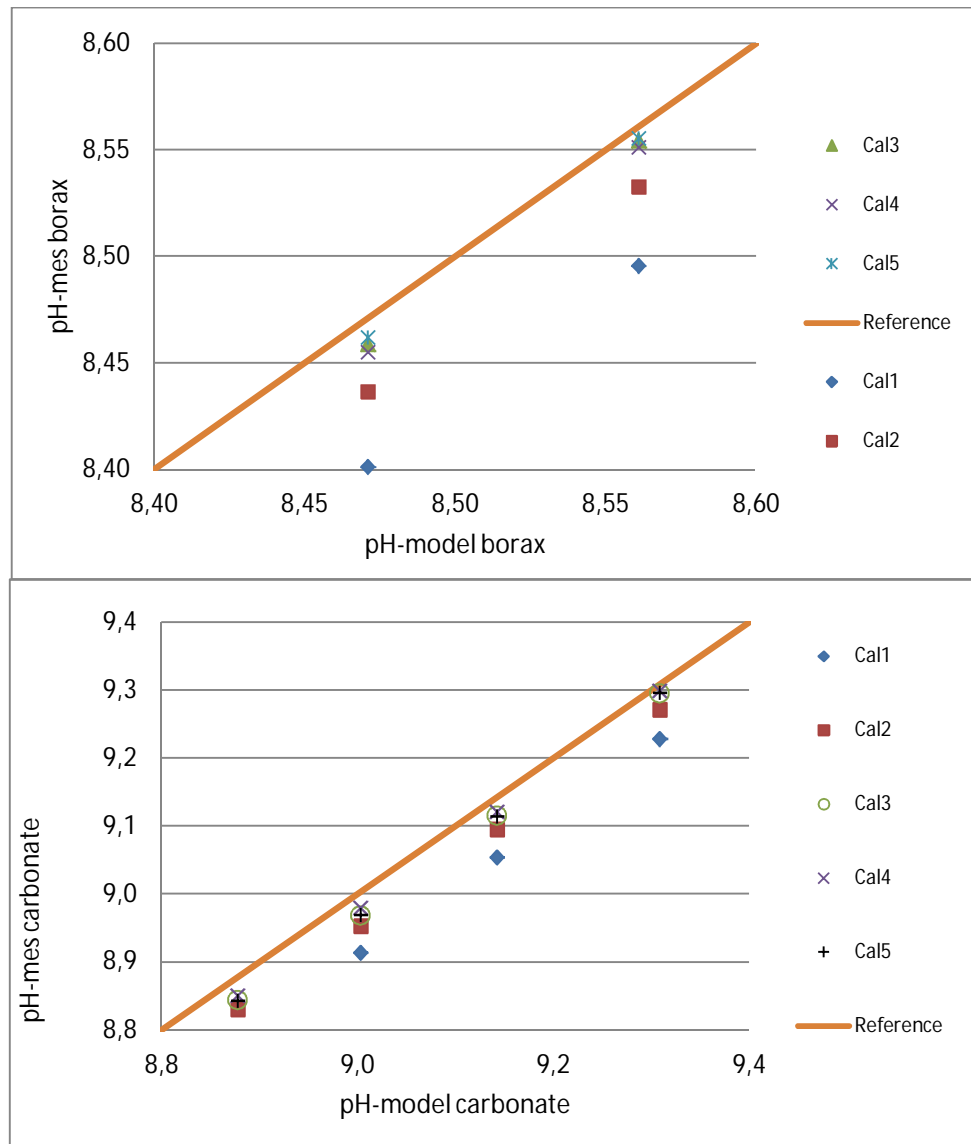
Figure 9. Modeled values plotted against measured values for carbonate and borax with varying NaCl calibrations

For borax the integral was calculated for the pH range between 8.4 and 8.6 and for carbonate between 8.8 and 9.4. The results are presented in Table 7.

Table 7.   Integral of NaCl calibrations

Calibration (Sample borax) [M (NaCl)]	$\int_{8.4}^{8.6} (x - (a + bx))^2 \; dx$
0	$1.000 \; 10^{-3}$
0.25	$3.485 \; 10^{-4}$
0.5	$7.642 \; 10^{-5}$
0.75	$6.808 \; 10^{-5}$
1	$6.093 \; 10^{-5}$
Calibration (Sample carbonate) [M (NaCl)]	$\int_{8.8}^{9.4} (x - (a + bx))^2 \; dx$
0	$5.000 \; 10^{-3}$
0.25	$2.000 \; 10^{-3}$
0.5	$7.206 \; 10^{-4}$
0.75	$3.475 \; 10^{-4}$
1	$5. \; 001 \; 10^{-4}$

The smallest value is obtained for 0.75M NaCl calibration for carbonate and 1M NaCl for borax samples. But it should be noted, that the difference between the 0.75M NaCl and 1M NaCl calibration is relatively small with borax samples. Also at lower ionic strengths (0.38 and 0.76) around 0.5 and 1xSW the 0.75M NaCl calibration yields more accurate pH measurements to the Pitzer-model as can be seen in Figure 7. Based on these results the 0.75M NaCl calibration was selected as most appropriate for both carbonate and borax.

The data in Figures 7 and 8 can also be found in Tables 11 and 12 in Appendix 3.

6.3   Experiment set 3

Samples with 0.0025M carbonate, 0.001M borax, synthetic SW at 1, 1.5, 2 and 2.5xSW and 0.1M HCl additions of 0, 3, 5, 7, 9 and 10 ml were measured with the Metrohm combined glass electrode. The electrode was calibrated with NIST secondary buffers phthalate, phosphate and carbonate prepared in 0.75M NaCl solution. Calibration with 0.75M NaCl was selected from the previous experiment as it gave good accuracy for pH measurements for the whole range of SW strengths. Sample pH was modelled with the Pitzer model and compared to measured values.

Results for measured and modelled samples are plotted in Figure 10 for samples 1xSW and 1.5xSW and in Figure 7 for samples 2xSW and 2.5XSW. pH measurement for sample 2.5xSW with 10mM is not presented due to an error made in the preparation of the sample. The 0.75M NaCl calibration yielded measurements within the desired 0.03 pH unit from the model for all different SW strengths with 0 ml HCl added. Compared to results from the first set of experiments, where standard calibration was used, a clear improvement for measurements made at higher ionic strengths can be seen with the new calibration. The accuracy of measurements generally decreased with added HCl but no linearity between added HCl and accuracy is visible. For example, for all SW strengths excluding 1xSW, the measurements at lower pH were sometimes more accurate with more HCl added than the previous sample with less HCl added. See Table 13 in Appendix 3 for SWx2 samples with 5 and 7 ml HCl added.

The results show that the Pitzer model has the ability to predict acid base interactions well. The measured values fit the Pitzer model with a reasonable accuracy. The accuracy of measured values is better for samples with less HCl added

Precipitation was observed on the surface of some samples when carbonate was added. When the samples were thoroughly mixed, the solids dissolved. All samples were mixed thoroughly before measurement. The precipitation observed in some samples was most likely cause by localized conditions in the flask. Perhaps incomplete mixing of the acid caused the surface of the sample to have a higher pH that caused precipitation.
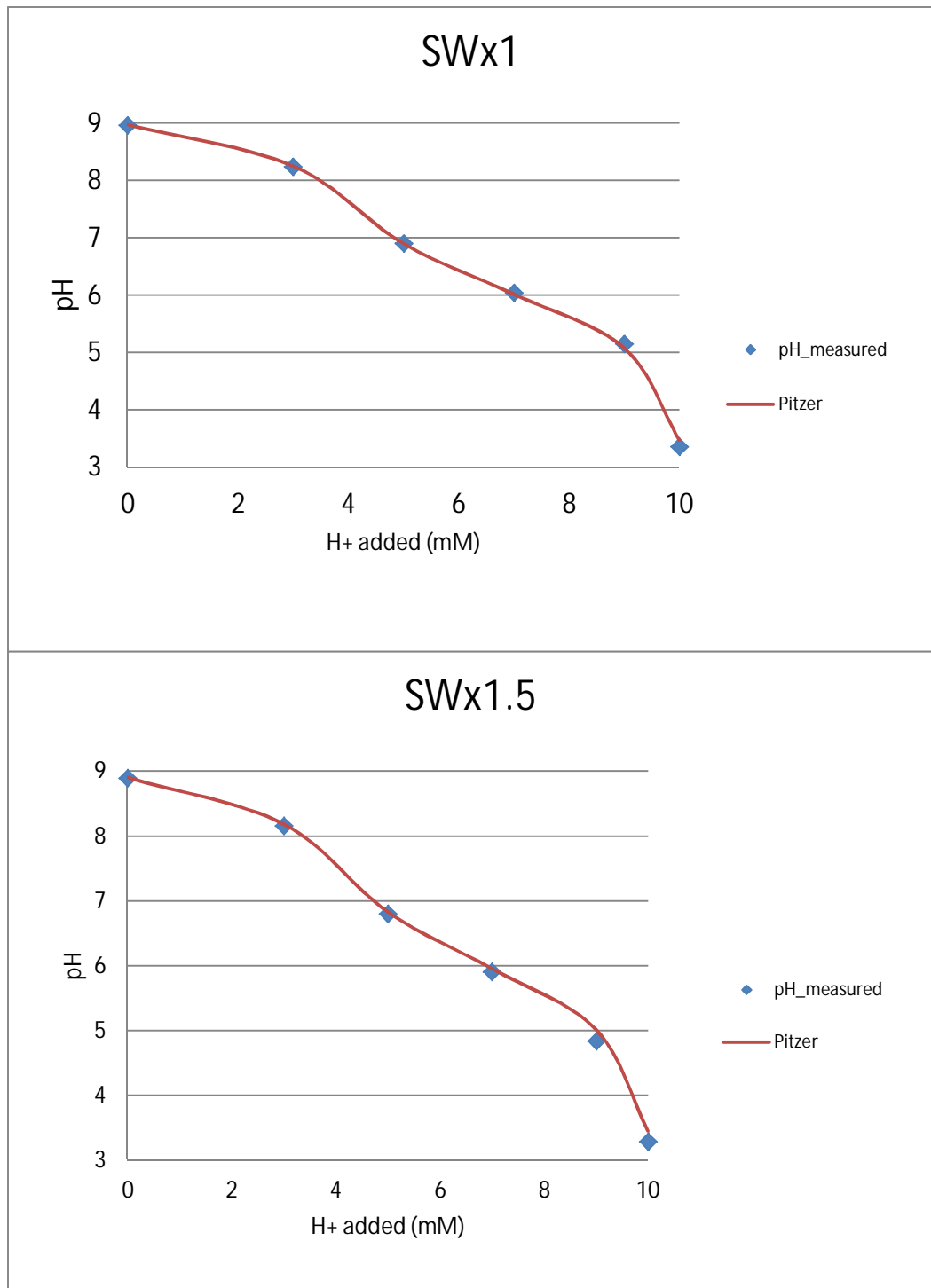
Figure 10. HCl added to acid-base samples with SWx1 and SWx1.5
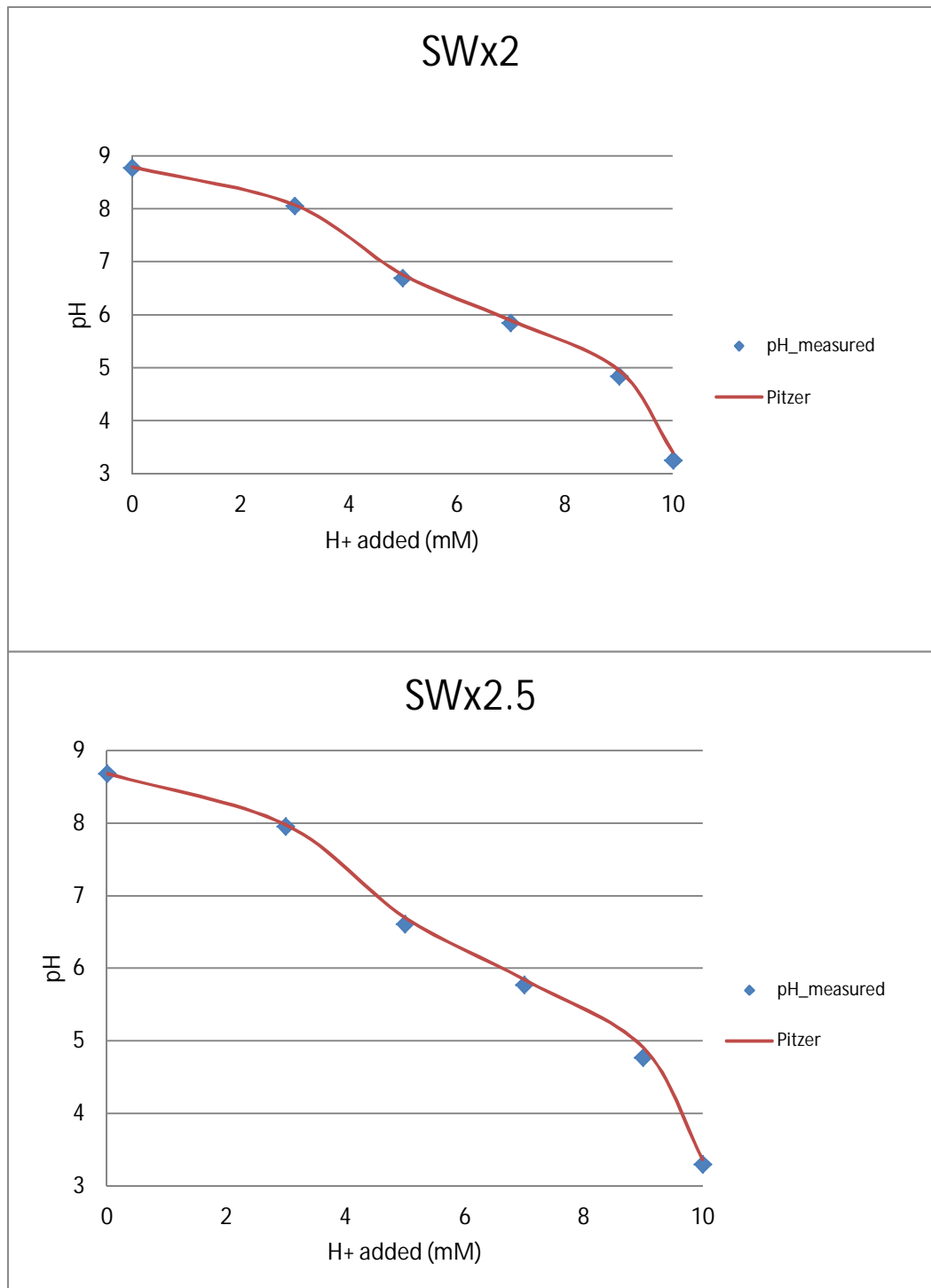
Figure 11.   HCl added to acid-base samples with SWx2 and SWx2.5

7   Estimation of errors

Possible sources of error in the experiments rise from methods used in preparation of samples and standards. Also environmental conditions affect the preparation of samples, standards and the actual pH measurements.

The preparation of samples and standards include weighing errors and volume errors. Weighing and volume errors effect the concentration and ionic strength of the solutions which directly affect the pH of the solutions. Weighing errors can, for example, be caused by salts absorbing moisture, air currents in the laboratory, calibration of analytical balance and carless handling of weighed salts. With proper working methods these errors can be reduced. In the experiments done in this thesis, $CaCl_2$ and $MgCl_2$ were for example extremely hydroscopic and thus difficult to weigh. This was taken into account by weighing the salts directly after drying.

All solutions were prepared on a volume basis for practical reasons. This is slightly less accurate than working with mass, as volume is temperature dependent, but care was taken to allow water to stabilize to room temperature before preparing solutions.

The ΔpH (modelled – measured pH values) includes volume and weighing errors. Negligible errors may be caused by the difference in actual molarity and modelled molarity. The models were run with the target molarity and not with the actual measured values from weighing. Nevertheless, the weighing and volume errors in this thesis work are estimated to be fairly small. This was observed by modelling the actual measured values, which did not have a significant difference to pH values modelled with target values. Prepared calibration buffers were also tested a few times against corresponding Merck certified calibration buffers. The difference between prepared buffers and certified Merck buffers was negligible (only 0.1 mv), which shows that the preparation of accurate solutions was possible in this work.

Part of the uncertainty in pH measurement is caused by the electrode itself, calibration and environmental conditions. The main environmental condition effecting pH measurement is temperature, but mixing can also affect the electrode response and should be kept constant. The overall uncertainties in pH values for this thesis work are given by average standard deviations. The average standard deviations for each experiment are listed in Table 8. It is important to note that the average standard deviations repre-

sent an upper limit for the total uncertainty, which includes measurement uncertainty and uncertainties from preparation of samples.

Table 8.   Estimation of overall experimental and measurement uncertainty

Experiment	Average standard deviation	Upper limit for uncertainty at 95%-confidence level
Experiment 1 (Borax)	0.010	±0.021
Experiment 1 (Carbonate)	0.013	±0.025
Experiment 2 (Borax)	0.007	±0.013
Experiment 2 (Carbonate)	0.005	±0.010
Experiment 3 (Acid additions)	0.072	±0.144

The uncertainty for the first set of experiments is slightly larger than for the second set of experiments. This is most likely caused by the cumulative weighing errors as weighed salts were added cumulatively to the sample solutions. This is observed in the standard deviations of experiment set 1, which increase as salts are added. The standard deviations for experiment set 2, with no NaCl added (basically same experiment as experiment set 1) are more constant and do not increase linearly with increase of salt concentration. The only difference between these measurements is that stock solutions were used for the second set of experiments eliminating the weighing errors observed in the first set of experiments. The considerably larger uncertainties for experiments set 3 are also reflective of experimental challenges. The low buffer capacity of the measured solutions increases the uncertainty of the measurements.

8   Discussion and Conclusions

The purpose of this thesis project was to test a new calibration method for a combined glass electrode to be used for measurements of high ionic strength brines. More accurate pH readings were needed for input into a single pass boron removal model, because errors caused by difference in liquid junction potential, in a standard NIST calibrated electrode and high ionic strength brines, were suspected to have a significant effect on the overall accuracy of the model. The goal for the new calibration was to improve accuracy of pH measurements in high ionic strength brines and for the measurements to be consistent with the Pitzer-based chemical equilibrium model with an accuracy of ±0.03 pH unit.

Three sets of experiments were carried out to achieve the goals. The first set of experiments was used to quantify difference of pH values, of varying ionic strength brines, obtained with the Pitzer model and pH values obtained with a standard NIST calibrated electrode. In other words, the aim was to verify and quantify the error in measuring high

ionic strength brines with a standard NIST calibrated electrode. The other two experiments were used to test if added NaCl to NIST calibration standards would yield more accurate pH measurements and how well the Pitzer model can predict acid-base reactions.

The results for borax and carbonate pH measurements made with NIST standard calibrated electrode in the first set of experiments show that the Pitzer model is in good agreement with measured pH values even at high ionic strengths. The Pitzer model is the best for the whole range of SW strengths tested. The differences between measured and modeled values for borax were lower than initially expected for SW and higher ionic strength solutions. The ΔpH for borax was 0.06 pH unit at most, compared to 0.1 pH unit that was initially estimated for ionic strengths comparable to SW. The differences between measured and modeled values for carbonate were closer to 0.1 pH unit all ready at SW ionic strengths.

The differences of measured results to the Pitzer model appear to become more constant with increasing ionic strength. With the SIT and Minteq4 the ΔpH keeps increasing with ionic strength. Borax measurements were slightly more accurate and replicate measurements had a smaller standard deviation than carbonate samples. This could be caused by experimental difficulties with measuring carbonate that is susceptible to CO_2 diffusion from the atmosphere. The absorbed CO_2 decreases the pH. It is also possible that experimental data for the Pitzer parameters for carbonate is not as extensive and could have larger uncertainties. This would lead to a larger difference between modeled and measured pH values.

The results from the first experiment verify a need for a more accurate pH measurement. It can also be concluded that RLJP-errors in pH measurements of high ionic strength brines made with an electrode calibrated with NIST standard calibration buffers can be up to 0.1 pH unit.

The second set of experiments show that adding NaCl to calibration standards has the ability to improve pH measurements made in synthetic SW and higher ionic strength brines. Measurements of borax and carbonate samples in synthetic SW and higher ionic strength solutions were improved with 0.5M, 0.75M or 1M NaCl additions to calibration standards. By adding NaCl to calibration standards the RLJP was reduced and measurements within 0.03 pH unit from the Pitzer model could be achieved for borax and carbonate samples in synthetic SW solutions up to 2.5xSW strength.

From the experiments carried out in this work it is difficult to conclude or define in more detail how the addition of NaCl affects the pH measurements. It seems that added NaCl has an effect only up to a certain concentration after which it is not possible to tell if there is a significant difference between the amounts added. The measured sample is also likely to have an effect on how much and how the added NaCl improves the measurement result. For example, 0.25M NaCl added to calibration standards already gives reasonably good results when measuring borax in SW solutions. More experiments and research would be needed to make more conclusions.

The final set of experiments was used to test the 0.75M NaCl calibration and see how well the Pitzer model can predict acid-base interactions. In this experiment borax and carbonate were both added to samples at concentrations that better represents concentrations in SW. The 0.75M NaCl calibration yielded good results for all samples with 0 ml HCl added. All of these measurements were under the desired 0.03 pH unit accuracy to the Pitzer model. This shows again that the NaCl calibrations are a clear improvement over the NIST standard calibration where the difference was up to 0.1 pH unit. At best, the improvement was up to one order in magnitude with the new calibration. The acid additions decreased the measurement accuracy but again the Pitzer model was a good representation of the experimental measurements.

The decrease in pH measurement accuracy with increase of added HCl could be caused by volume errors and low buffer capacity or general difficulty of the experimental setup. A calculation done in PHREEQC software showed that a 3% volume error in added H^+ could account for even the largest differences between measured pH and the Pitzer model. This is not to say that the volume errors are expected to be so large in this experiment, but depending on the pipette and temperature of the solution, it could easily be between 1-2%. Atmospheric CO_2 interaction with the sample solution can also be a source of measurement errors in this experiment. These errors are magnified in solution with low buffer capacity and cause unstable readings. The effect of CO_2 interaction was tried to avoid by adding carbonate to the sample immediately before taking the measurement. This method did not completely remove problems either, as sometimes it could take up to a few minutes for the sample temperature to reach equilibrium with the water bath. A closed measurement vessel with minimal head space was tested, but this did not seem to improve results, possibly indicating that the CO_2 effect may not be very large and that the source for error lies elsewhere.

As final conclusion, the experiments done in this thesis project are a good basis and show that more accurate and consistent pH measurements, with the Pitzer model, of high ionic strength brines can be obtained by simply reducing the RLJP. This is done by adding the main salt component of the test solution to the calibration standards. Using the Pitzer model for assigning pH values to modified calibration standards provides a simple means to improve pH measurement accuracy in high ionic strength brines that could be easily adopted in many industrial measurement applications. Further research and experimentation would be needed for wide scale adaptation of this type of calibration. The wide scale use of this type of calibration is also limited at the moment by the uncertainties in the Pitzer model itself, and thus a full uncertainty statement for the measurements cannot be given.

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Merck calibration standard certificates

Certificate of Analysis

Certipur® Reference Material

Certified Secondary Standard Reference Buffer Solution
pH(S)= 4.00₅ (25°C)
Potassium Hydrogen Phthalate

1.07200.0105   **Lot. No. HC253621**

This certificate of analysis is based on the data from the accredited Merck Calibration Laboratory for pH value and electrolytic conductivity, according to DIN EN ISO / IEC 17025.

Directly traceable to Primary   Potassium hydrogen phthalate
Reference Materials: from PTB and NIST

Lot no: PTB PHT-232/30251/12
                                     NIST 185 h

Measurement:
Directly measured by differential potentiometry with the aid of two platinum hydrogen electrodes „quasi without transference" against solutions prepared from primary reference materials from PTB[1] and NIST[2],

PTB1) : Physikalisch-Technische Bundesanstalt, Braunschweig, Germany
NIST2) : National Institute of Standards and Technology, Gaithersburg, USA

Measurement   ± 0.003 (5°C - 37°C)
Uncertainty: ± 0.004 (40°C - 50°C)

Table of pH(S) values, valid exclusively for lot no HC253621:

T [°C]	pH	T[°C]	pH
5.0	4.004	30.0	4.015
10.0	3.999	37.0	4.028
15.0	3.999	40.0	4.035
20.0	4.003	45.0	4.047
25.0	4.008	50.0	4.061

Date of release: 2012/11/21

Minimum shelf life: 2015/11/30

A. Yildirim

Dipl.-Ing. Ayfer Yildirim
(responsible laboratory manager quality control)

Merck KGaA · Frankfurter Straße 250, 64293 Darmstadt, Germany: + 49 6151 72-0

EMD Millipore Corp. · 290 Concord Road, Billerica, MA 01821, USA: +1-781-533-6000

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Certificate of Analysis

Certipur® Reference Material

Certified Secondary Standard Reference Buffer Solution
pH(S)= 6.86₃ (25°C) Potassium dihydrogen
phosphate/Disodium hydrogen phosphate

1.07202.0105   **Lot. No. HC253626**

This certificate of analysis is based on the data from the accredited Merck Calibration Laboratory for pH value and electrolytic conductivity, according to DIN EN ISO / IEC 17025.

Directly traceable to Primary Reference Materials: Potassium dihydrogen phosphate / Disodium hydrogen phosphate from PTB and NIST

Lot no: PTB-PHOA-155/1181/08
NIST 186 I+II g

Measurement:
Directly measured by differential potentiometry with the aid of two platinum hydrogen electrodes „quasi without transference" against solutions prepared from primary reference materials from PTB[1] and NIST[2],

PTB1) : Physikalisch-Technische Bundesanstalt, Braunschweig, Germany
NIST2) : National Institute of Standards and Technology, Gaithersburg, USA

Measurement   ± 0.003 (5°C - 37°C)
Uncertainty: ± 0.004 (40°C - 50°C)

Table of pH(S) values, valid exclusively for lot no HC253626:

T [°C]	pH	T[°C]	pH
5.0	6.952	30.0	6.853
10.0	6.924	37.0	6.843
15.0	6.901	40.0	6.839
20.0	6.882	45.0	6.836
25.0	6.866	50.0	6.835

Date of release: 2012-04-12

Minimum shelf life: 2015-04-30

A. Yildirim

Dipl.-Ing. Ayfer Yildirim
(responsible laboratory manager quality control)

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Certificate of Analysis

Certipur® Reference Material

Certified Secondary Standard Reference Buffer Solution pH(S)= 9.18_4 (25°C) di-sodium tetraborate decahydrate

1.07203.0105   **Lot. No. HC249424**

This certificate of analysis is based on the data from the accredited Merck Calibration Laboratory for pH value and electrolytic conductivity, according to DIN EN ISO / IEC 17025.

Directly traceable to Primary Reference Materials:	Sodium Tetraborate Decahydrate from PTB and NIST
Lot no:	PTB-BO-211/30002/11 NIST 187 e

Measurement:
Directly measured by differential potentiometry with the aid of two platinum hydrogen electrodes „quasi without transference" against solutions prepared from primary reference materials from PTB[1] and NIST[2],
PTB1) : Physikalisch-Technische Bundesanstalt, Braunschweig, Germany
NIST2) : National Institute of Standards and Technology, Gaithersburg, USA

Measurement Uncertainty:	± 0.003 (5°C - 37°C) ± 0.004 (40°C - 50°C)

Table of pH(S) values, valid exclusively for lot no HC249424

T [°C]	pH	T[°C]	pH
5.0	9.389	30.0	9.141
10.0	9.329	37.0	9.093
15.0	9.275	40.0	9.074
20.0	9.226	45.0	9.044
25.0	9.181	50.0	9.018

Date of release:	2012-03-20
Minimum shelf life:	2015-03-31

A. Yildirim

Dipl.-Ing. Ayfer Yildirim
(responsible laboratory manager quality control)

Merck KGaA · 64271 Darmstadt, Germany · Tel.: +49 (0) 6151 72 0
EMD Chemicals Inc., One Int. Plaza, Suite 300 · Philadelphia, PA 19113, USA, Tel. 1-888-367-3275

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Certificate of Analysis

Certipur® Reference Material

Certified Secondary Standard Reference Material
pH(S)= 10.01_4 (25°C) Sodium hydrogen carbonate/
Sodium carbonate

1.01962.0001   **Lot. No. 111962A**

This certificate of analysis is based on the data from the accredited Merck Calibration Laboratory for pH value and electrolytic conductivity, according to DIN EN ISO / IEC 17025.

Cat. No:	**1.01962.0001 (2.72071 + 2.72072)**
Lot. No:	**111962A (K42495171 + A854772)**

Directly traceable to Primary   Sodium hydrogen carbonate /Sodium carbonate
Reference Materials: from PTB and NIST

Lot no: PTB CAR-210/30001/11
                                                              NIST 191 d

Preparation:
Dry sodium carbonate for 90 minutes at 250°C and preserve over dry calcium chloride. Dry sodium hydrogen carbonate for 2 days over molecular sieve. Dissolve 2.640g of sodium carbonate and 2.092g of sodium hydrogen carbonate in 800 ml water and make up to 1000ml at 25°C. **The solution is sensitive to carbon dioxide**

Measurement:
The sodium hydrogen carbonate/sodium carbonate solution was dirctly measured against identically prepared solutions of primary reference material from PTB1) and NIST2) by differential potentiometry with the aid of two platinum hydrogen electrodes
"quasi without transference".

PTB1) : Physikalisch-Technische Bundesanstalt, Braunschweig, Germany
NIST2) : National Institute of Standards and Technology, Gaithersburg, USA

Date of release:	2011-12-14
Minimum shelf life:	2015-12-31

A. Yildirim

Dipl.-Ing. Ayfer Yıldırım
(responsible laboratory manager quality control)

Helsinki
Metropolia
University of Applied Sciences

**Measurement
Uncertainty:**

± 0.003 (5°C - 37°C)
± 0.004 (40°C - 50°C)

Table of pH(S) values, valid exclusively for lot no 111962A:

T [°C]	pH	T[°C]	pH
5.0	10.251	30.0	9.970
10.0	10.179	37.0	9.914
15.0	10.117	40.0	9.891
20.0	10.062	45.0	9.855
25.0	10.013	50.0	9.824

Measurement Uncertainty:
The expanded uncertainty U in the certified value is calculated in accordance to GUM and EA-4/02 as $U = k \cdot u_c$ where $k = 2$ is the coverage factor for a 95% coverage probability. The combined uncertainty u_c is obtained from the contributions of the primary reference material, the temperature and the measuring system.

Quality Management System:
This CertiPUR® Reference Material has been prepared and certified under an ISO 9001 quality management system in accordance to the following guides.

General requirements for the competence of testing and calibration laboratories	DIN EN ISO / IEC 17025: 2005
Guide to the Expression of Uncertainty in Measurement	GUM: 1995
Expression of the Uncertainty of Measurement in Calibration	EA-4/02: 1999
Quantifying Uncertainty in Analytical Measurement	EURACHEM / CITAC: 2000
Reference Materials - Contents of certificates and labels	ISO Guide 31: 2000
Guideline for the requirements for the competence of reference materials producers	ILAC G12: 2000

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NIST recipe for borax

Directions for Use

Preparation of the 0.01-molal solution: Crush gently any large lumps of salt. The salt must not be dried in an oven before use. Transfer 3.81g of the borax to a flask and dissolve in 1.000 kg of distilled carbon dioxide-free water. Alternatively, if volumetric apparatus is to be used, transfer 3.80g to a 1-liter volumetric flask, dissolve in distilled carbon dioxide-free water, and fill to the mark with water at 25 °C. Water, sufficiently carbon dioxide-free, can be prepared by boiling for 10 min. and cooling in a vessel guarded by a soda-lime tube. The water should have a conductance less than $2 \times 10^{-6}\,ohm^{-1}\,cm^{-1}$. To avoid contamination of the buffer solution with atmospheric carbon dioxide, keep the stopper in place except when removing a portion of the solution. If desired, the solution may be protected with a soda-lime tube. Prepare fresh solutions at least once a month. For the highest accuracy, prepare fresh solutions on a weekly basis.

°C	pH(S)	°C	pH(S)	°C	pH(S)
0.0	9.463	20.0	9.226	40.0	9.070
5.0	9.395	25.0	9.180	45.0	9.042
10.0	9.333	30.0	9.139	50.0	9.018
15.0	9.277	35.0	9.102		

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Tables of experimental results

Table 9.   Modeled and average pH for borax at varying SW strengths

Salts [xSW]	pH_Pitzer	pH_SIT	pH_minteqV4	pH_measured_av.	STDEV	ΔpH
0	9.176	9.203	9.169	9.194	0.002	-0.018
0.1	9.085	9.112	9.059	9.065	0.003	0.020
0.5	8.911	8.958	8.838	8.863	0.004	0.048
1	8.777	8.852	8.642	8.717	0.004	0.060
1.5	8.673	8.775	8.461	8.613	0.006	0.059
2	8.584	8.714	8.281	8.524	0.012	0.060
3	8.431	8.616	7.902	8.376	0.010	0.055
4	8.297	8.539	7.498	8.240	0.019	0.056
5	8.172	8.476	7.076	8.124	0.017	0.048

Table 10.   Modeled and average pH for carbonate at varying SW strengths

Salts [xSW]	pH_Pitzer	pH_SIT	pH_minteqV4	pH_measured_av.	STDEV	ΔpH
0	10.006	9.851	9.856	10.012	0.003	-0.006
0.1	9.874	9.689	9.705	9.847	0.005	0.026
0.5	9.544	9.382	9.408	9.476	0.007	0.068
1	9.318	9.221	9.229	9.230	0.009	0.088
1.5	9.161	9.126	9.104	9.062	0.011	0.098
2	9.033	9.060	9.005	8.929	0.013	0.105
3	8.822	8.968	8.857	8.712	0.015	0.110
4	8.639	8.905	8.759	8.531	0.018	0.108
5	8.470	8.858	8.692	8.372	0.021	0.098

Table 11.   Borax pH measured with different NaCl calibrations

X SW Strength	Cal1_0NaCl	Cal2_0.25NaCl	Cal3_0.5NaCl	Cal4_0.75NaCl	Cal5_1NaCl
Borax0	9.199	9.244	9.263	9.267	9.270
Borax0.5	8.871	8.913	8.933	8.934	8.940
Borax1	8.719	8.759	8.780	8.780	8.786
Borax1.5	8.598	8.638	8.659	8.658	8.663
Borax2	8.495	8.533	8.554	8.551	8.555
Borax2.5	8.401	8.437	8.459	8.455	8.462
X SW Strength	**STDEV1**	**STDEV2**	**STDEV3**	**STDEV4**	**STDEV5**
Borax0	0.008	0.004	0.004	0.001	0.005
Borax0.5	0.010	0.003	0.001	0.004	0.004
Borax1	0.013	0.005	0.003	0.007	0.002
Borax1.5	0.013	0.005	0.002	0.007	0.004
Borax2	0.014	0.006	0.004	0.007	0.002
Borax2.5	0.012	0.004	0.003	0.007	0.005
X SW Strength	**ΔpH1**	**ΔpH2**	**ΔpH3**	**ΔpH4**	**ΔpH5**
Borax0	-0.019	-0.065	-0.084	-0.087	-0.090
Borax0.5	0.039	-0.003	-0.023	-0.024	-0.030
Borax1	0.038	-0.002	-0.023	-0.023	-0.029
Borax1.5	0.061	0.021	0.000	0.001	-0.004
Borax2	0.066	0.028	0.007	0.010	0.006
Borax2.5	0.070	0.034	0.012	0.016	0.009

Table 12.   Carbonate pH measured with different NaCl calibrations

X SW Strength	Cal1_0NaCl	Cal2_0.25NaCl	Cal3_0.5NaCl	Cal4_0.75NaCl	Cal5_1NaCl
Carbonate0	10.005	10.054	10.080	10.088	10.087
Carbonate0.5	9.473	9.520	9.544	9.550	9.548
Carbonate1	9.228	9.271	9.294	9.298	9.296
Carbonate1.5	9.053	9.095	9.115	9.121	9.114
Carbonate2	8.913	8.953	8.968	8.979	8.968
Carbonate2.5	8.791	8.830	8.844	8.850	8.843
X SW Strength	**STDEV1**	**STDEV2**	**STDEV3**	**STDEV4**	**STDEV5**
Carbonate0	0.002	0.006	0.002	0.006	0.009
Carbonate0.5	0.006	0.007	0.005	0.004	0.008
Carbonate1	0.005	0.003	0.004	0.002	0.005
Carbonate1.5	0.002	0.003	0.002	0.008	0.006
Carbonate2	0.004	0.003	0.006	0.005	0.006
Carbonate2.5	0.006	0.002	0.006	0.004	0.007
X SW Strength	**ΔpH1**	**ΔpH2**	**ΔpH3**	**ΔpH4**	**ΔpH5**
Carbonate0	0.003	-0.045	-0.071	-0.080	-0.078
Carbonate0.5	0.068	0.022	-0.003	-0.009	-0.007
Carbonate1	0.081	0.037	0.014	0.010	0.013
Carbonate1.5	0.089	0.048	0.028	0.022	0.029
Carbonate2	0.090	0.051	0.036	0.025	0.035
Carbonate2.5	0.087	0.048	0.034	0.028	0.035

Table 13.   HCl additions to samples solutions

synt seawaterx1 + buffers			
H+ added (mM)	pH_measured1	pH pitzer	∆pH
0	8.972	8.978	0.006
3	8.243	8.256	0.013
5	6.905	6.902	-0.003
7	6.048	6.019	-0.029
9	5.153	5.080	-0.073
10	3.354	3.475	0.121
synt seawaterx1.5 + buffers			
H+ added (mM)	pH_measured1	pH pitzer	∆pH
0	8.894	8.909	0.015
3	8.16	8.189	0.029
5	6.802	6.831	0.029
7	5.905	5.958	0.053
9	4.832	5.019	0.187
10	3.284	3.450	0.166
synt seawaterx2 + buffers			
H+ added (mM)	pH_measured1	pH pitzer	∆pH
0	8.778	8.796	0.018
3	8.056	8.083	0.027
5	6.695	6.768	0.073
7	5.854	5.903	0.049
9	4.846	4.965	0.119
10	3.262	3.413	0.151
synt seawaterx2.5 + buffers			
H+ added (mM)	pH_measured1	pH pitzer	∆pH
0	8.682	8.692	0.010
3	7.959	7.985	0.026
5	6.613	6.707	0.094
7	5.773	5.851	0.078
9	4.774	4.914	0.140

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Regression analysis for experiment set 1

Borax

Pitzer
SUMMARYOUTPUT

Regression Statistics	
Multiple R	0.998625495
R Square	0.997252879
Adjusted R Square	0.996860433
Standard Error	0.020332031
Observations	9

ANOVA

	df	SS	MS	F	Significance F
Regression	1	1.050478284	1.050478	2541.122267	3.16569E-10
Residual	7	0.00289374	0.000413		
Total	8	1.053372025			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-0.491110868	0.181169825	-2.71078	0.030165132	-0.91950943	-0.06271
X Variable 1	1.05160344	0.020861197	50.40955	3.16569E-10	1.002	1.100932

SIT
SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.998504
R Square	0.99701
Adjusted R Square	0.996583
Standard Error	0.021211
Observations	9

ANOVA

	df	SS	MS	F	Significance F
Regression	1	1.050223	1.050223	2334.359	4.26E-10
Residual	7	0.003149	0.00045		
Total	8	1.053372			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-4.09625	0.263603	-15.5395	1.1E-06	-4.71957	-3.47293
X Variable 1	1.445926	0.029927	48.3152	4.26E-10	1.37516	1.516692

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Minteq4
SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.970803
R Square	0.942458
Adjusted R Square	0.934237
Standard Error	0.093054
Observations	9

ANOVA

	df	SS	MS	F	Significance F
Regression	1	0.992759	0.992759	114.6495	1.36E-05
Residual	7	0.060614	0.008659		
Total	8	1.053372			

	Coefficient	Standad Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	4.517948	0.38577	11.7111	7.49E-06	3.605748	5.4309
X Variable 1	0.494556	0.04618	10.7075	1.36E-05	0.385338	0.6033

Carbonate

Pitzer
SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.999427982
R Square	0.998856291
Adjusted R Square	0.998692904
Standard Error	0.020513055
Observations	9

ANOVA

	df	SS	MS	F	Significance F
Regression	1	2.572446156	2.572446	6113.439091	1.47309E-11
Residual	7	0.002945498	0.000421		
Total	8	2.575391654			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-0.702431684	0.12593917	-5.57755	0.000835375	-1.0002305	-0.40463
X Variable 1	1.067900018	0.013658022	78.18848	1.47309E-11	1.036	1.100196

SIT
SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.983652
R Square	0.967572
Adjusted R Square	0.962939
Standard Error	0.109228
Observations	9

ANOVA

	df	SS	MS	F	Significance F
Regression	1	2.491876	2.491876	208.86	1.81E-06
Residual	7	0.083516	0.011931		
Total	8	2.575392			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-5.64681	1.023126	-5.51917	0.000888	-8.06612	-3.2275
X Variable 1	1.601142	0.11079	14.45199	1.81E-06	1.339165	1.86312

Minteq4
SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.99695
R Square	0.99391
Adjusted R Square	0.99304
Standard Error	0.047334
Observations	9

ANOVA

	df	SS	MS	F	Significance F
Regression	1	2.559708	2.559708	1142.48	5.14E-09
Residual	7	0.015683	0.00224		
Total	8	2.575392			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	-3.54392	0.375294	-9.44305	3.12E-05	-4.43135	-2.65649
X Variable 1	1.380695	0.040848	33.80059	5.14E-09	1.284104	1.477286

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