

#### Produced water chemistry - Analysis of produced water from the Danish North Sea: Inorganic ions, heavy metals and organic compounds

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# **Produced water chemistry**

Analysis of produced water from the Danish North Sea: Inorganic ions, heavy metals and organic compounds

# PhD thesis

Sofie Nitsche Bergfors



"Det har jeg aldrig prøvet før, så det klarer jeg helt sikkert!" *"I've never tried it before, so I'm sure I can!"* - Pippi Langstrømpe

### Produced water chemistry

Analysis of produced water from the Danish North Sea: Inorganic ions, heavy metals and organic compounds

PhD thesis September, 2020

### By Sofie Nitsche Bergfors

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### Preface

This thesis was prepared at the Centre for Oil and Gas at the Technical University of Denmark (DTU) in the period from September 2016 to September 2020. It is submitted in partial fulfilment of the requirements for acquiring the degree of Doctor of Philosophy (Ph.D.) in Chemistry. The work has been followed and will be evaluated by the PhD School at DTU Chemistry. Parts of the work has been prepared at a partner research centre, Geological Survey of Denmark and Greenland (GEUS).

Senior Researcher Karen L. Feilberg (Centre for Oil and Gas - DTU) was the principal supervisor of the project. Additionally, Senior Researcher Wei Yan (DTU Chemistry) and Senior Researcher Niels H. Schovsbo (GEUS) both functioned as co-supervisors of the project.

The project was fully funded by the Danish Hydrocarbon Research and Technology Centre (DHRTC) as part of the Advanced Water Flooding - 1 (AWF.1) flagship program. All samples and data included are from TOTAL (Mærsk Oil and Gas until 2018). The Danish Underground Consortium (DUC) consisting of TOTAL, Noreco and Nordsøfonden has provided permission to publish this work.

Sofie Nitsche Bergfors - s170034

Signature

Date

## Abstract

Water constitutes approximately half of the fluid volume produced at part of the oil production in the Danish North Sea. The presented PhD study examines the chemical composition of produced water, both experimentally and computationally, to shred light on the temporal and regional variations in the water composition. The findings are discussed in a context of production strategies, scale and corrosion mitigation strategies and adds to a pure geochemical understanding. Included in the study are the fours fields: Dan, Halfdan, Kraka and Valdemar. At Dan and Halfdan, seawater is injected for improved oil recovery and pressure support, but the accompanying consequences for reservoir quality and the potential for further recovery are not fully evaluated. Also, a need for a more sensitive analytical workflow for the analysis of Ba<sup>2+</sup> has been identified for an accurate prediction of hard scale formation.

Principal component analysis is used to study an extensive data set for the four included fields covering the produced water chemistry (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Cl<sup>-</sup> and  $SO_4^{2-}$ ) from start of production up to and including 2015. Five water types are classified; these differ mainly by salinity and the concentration of the divalent ions. These are used as input for scale predictive calculations, which show a high risk of potential hard scale formation in many wells. Additionally, the findings suggest a connectivity between the close-lying fields, Dan and Halfdan. The quality of the data set discussed above has been examined experimentally from a comparison between data and new analytical results of similar samples; the Halfdan field was used as a case study. For this purpose, and to improve the analytical sensitivity for all ions, but especially Ba<sup>2+</sup>, a new analytical workflow is introduced utilising the benefits of inductively coupled plasma - optical emission spectroscopy (ICP-OES). This is combined with routine analysis of the included anions using ion chromatography. In short, good agreement between data and new results were observed. This was confirmed by an inter-laboratory and inter-instrumental test. The analytical workflow using ICP-OES showed an increased sensitivity for all cations and provided accurate measurements of the  $Ba^{2+}$  concentrations despite the high salinity matrix which is an inevitable condition of in the produced water samples. This is extremely valuable for future analysis of produced water; for example for the study of (exchange) mechanisms in the reservoirs and in the prediction of scale formation. A study of changes in produced water chemistry as a consequence of sample storage suggested no major changes, thus proving the value of stored samples for many purpose, eq. barium scale prediction. By the use of inductively coupled plasma - mass spectrometry (ICP-MS), the content of five heavy metal ions ( $Mn^{2+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$ ,  $Hg^{2+}$  and  $As^{2+}$ ) were studied in a subset of samples including samples from the Halfdan, Kraka and Valdemar fields, as these three fields showed the largest produced water composition variations. The acquired results showed a clear distinction between the fields based on the concentration of the heavy metals ions. Last, comprehensive two-dimensional gas chromatography (GCxGC-HRMS) is used for a non-target screening study of dissolved organic species in produced water samples from the Halfdan field. 18 distinct organic compounds are observed, including alcohols and saturated and aromatic acids. Further analysis of the achieved results from this study may yield some interesting geographical differences.

We successfully classified five types of produced water from the Dan, Halfdan, Kraka and Valdemar field, which are used as input for decision making on production strategies, and scale and corrosion prediction and mitigation strategies. The water types also add input to geochemical studies. The findings are confirmed by an experimental study, which presents a new analytical workflow that was successfully developed and validated for the analysis of produced water samples - combining the benefits of ICP-OES and IC. A study of heavy metals ions in the produced water suggests that the concentrations of these also display regional variations; thus linking the heavy metal ions to the classified water types. A presented experimental technique for the analysis of dissolved organic species in produced water shows great potential and may be taken further.

### Resumé

Vand udgør cirka halvdelen af det volumen af væske der produceres i forbindelse med olieudvindingen i den danske sektor af Nordsøen. I dette PhD studie studeres den kemiske sammensætning af det producerede vand, både eksperimentelt og ved avanceret data analyse, for at belyse regionale såvel som tidsmæssige ændringer i vandsammensætningen. De opnåede resultater bliver diskuteret både i forhold til produktionsstrategier, strategier til at mindste risikoen for udfældninger og korrosion. Endeligt føder resultaterne også ind til geokemiske studier. Fire felter fra den danske Nordsø er inkluderet i dette studie: Dan, Halfdan, Kraka og Valdemar. Olieproduktion på Dan og Halfdan er opretholdt ved hjælp fra vandinjektion. De dertil følgende konsekvenser og et eventuelt potentiale for øget produktion er ikke tilstrækkeligt udredt. Ydermere har dette studie vist at der er et udtalt behiv for at Ba<sup>2+</sup> kan detekteres mere præcist for at muliggøre en mere præcis forudsigelse af eventuel dannelse af hård skæl.

Hovedkomponentsanalyse (PCA) anvendes i dette studie til at analysere et omfattende datasæt indeholdende information om den kemiske sammensætning af produktionsvand (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Cl<sup>-</sup> og SO<sub>4</sub><sup>2-</sup>) helt fra produktionens begyndelse og op til 2015. I alt er fem vandtyper klassificeret; disse varierer primært i forhold til deres totale salinitet og koncentrationerne af de divalente ioner. De identificerede vandtyper er input til risikoberegninger for udfældninger, hvilket viser en høj risiko for dannelse af de uopløselige belægninger SrSO<sub>4</sub> og BaSO<sub>4</sub>. Fra vandtyperne kan der ydermere identificeres en forbindelse mellem vandtyperne på de tætliggende felter Dan og Halfdan. Data fra ovennævnte studie er undersøgt i et detaljeret og højpræcist eksperimentelt studie. Halfdanfeltet blev anvendt som casestudie. I dette eksperimentelle studie introduceres induktivt koblet plasma - optisk emissionsspektroskopi (ICP-OES), idet metoden kan bidrage med en øget sensitivitet, som er vigtigt i analysen af alle ioner, og særligt Ba $^{2+}$ . Metoden kombinerer ICP-OES med ionkromatografi til analyse af de inkluderede anioner. Helt overordnet, observerer vi en god overensstemmelse mellem data og de nye eksperimentelle resultater. Dette blev bekræftet af både inter-laboratorie og inter-instrumentel sammenligningsstudier. Det nye workflow, inkluderende ICP-OES, udviste øget sensitivitet overfor alle kationer, også  $Ba^{2+}$ , trods den meget salte baggrundsmatrix der er et uundgåeligt vilkår ved analyse of produktionsvand. Dette er ekstremt brugbart ved fremtidige analyser af produktionsvand; eksempelvis til at studere udvekslingsmekanismer mellem kationer og i forudsigelsen af udfældninger. Eventuelle ændringer i sammensætningen af produktionsvandet som konsekvens af opbevaring over tid blev studeret og ingen særligt betydningsfulde ændringer blev observeret. Dette påviser at prøverne beholder deres værdi på trods af at de har stået opbevaret over længere tid. Induktivt koblet plasma - massespektrometri (ICP-MS) blev anvendt til at studere et muligt indhold af tungmetal ioner (Mn<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Hg<sup>2+</sup> and As<sup>2+</sup>) i det producerede vand. Prøver fra felterne Halfdan, Kraka og Valdemar var inkluderet i dette studie, idet en stor variation i produktionsvandet fra disse felter er observeret. Resultaterne herfra viste en klar forskel mellem felterne baseret på indholdet af tungmetalliske ioner. Endeligt blev todimensionel gaskromatografi koblet til et højtopløseligt massespektrometer anvendt i et non-target screening studie af opløste organiske forbindelser i produktionsvandsprøver fra Halfdanfeltet. I alt blev 15 forskellige organiske forbindelser identificeret i alle de inkluderede prøver. Disse omfatter alkoholer, mættede og aromatiske syrer. Et studie over regionale forskelle er en spændende mulighed, men kræver yderligere databehandling.

Vi har med succes klassificeret fem forskellige vandtyper fordelt over de fire felter Dan, Halfdan, Kraka og Valdemar. Disse bruges som input til beslutningstagere i forbindelse med produktionsstrategier, forudsigelse af udfældnigner og korrosion, og den følgende mulighed for at undgå dannelse heraf så vidt muligt. Vandtyperne føder også ind til en øget forståelse for geokemien i oliereservoirerne. Resultaterne er positivt bekræftet af et eksperimentelt studie, hvori det også fremlægges en ny, valideret, analytisk proces for analysen of produktionsvand ved brug af ICP-OES og IC i kombination. Et studie dækkende indholdet of tungmetal-ioner i produktionsvandet indikerer også regionale forskelle. Dette forbinderr de tungmetalliske ioner til de klassificerede vandtyper. Slutteligt, finder vi at den præsenterede teknik for analyse af opløste organiske forbindelser i produktionsvand har potentiale til at være en robust metode til at karakterisere syrer og alkoholler opløst i vandfasen.

### Acknowledgements

I would like to thank all the people without whom this work would not have been possible.

First, my supervisor Karen L. Feilberg who have been covering my back throughout the project and to guide me to the right specialists.

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I thank Wei Yan for being there at need. I am indebted to Charlotte Lassen, who have pointed me to the right specialists and helped me grant access to the data needed.

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DHRTC is thanked for the full funding, and the many opportunities that have followed along. I am also grateful for all my current and former colleagues at the Center for Oil and Gas - DTU, who have helped me making the days run and with overcoming the small daily challenges.

My father, Finn. R. Gottfredsen, is thanked for proofreading of this thesis; and for being my mentor from first grade all up til now.

Finally, I would like to express my deepest appreciation to my husband for this unwavering support. Even when I had no belief left, you trusted me.

> Sofie Nitsche Bergfors M.Sc. in Chemistry

### **List of Publications**

This Ph.D. thesis is based on the work described in the following papers and manuscript drafts:

- Sofie N. Bergfors, Niels H. Schovsbo, Karen L. Feilberg. Classification of and changes within formation water types in Danish North Sea Chalk: A study of the Halfdan, Dan, Kraka and Valdemar oil reservoirs. Applied Geochemistry. **122**, 104702, p. 1-16, 2020
- 2. <u>Sofie N. Bergfors</u>, Simon I. Andersen, Karen L. Feilberg. *Produced water from the North Sea – A case study and analytical guidelines*. Submitted to Journal of Separation Science, September 2020.
- 3. Sofie N. Bergfors, Simon I. Andersen, Karen L. Feilberg. *Produced water from the* North Sea A case study and analytical guidelines. Part 2: Impact of storage. To be submitted to Journal of Separation Science.

Publications related to the Ph.D. topic, but not included in the thesis:

- Niels H. Schovsbo, Hanne D. Holmslykke, Claus Kjøller, Lars E. Kristensen, Kim Esbensen, Amalia Y. Halim, <u>Sofie N. Gottfredsen</u>, Karen L. Feilberg, Sidsel M. Nielsen. Decoding the water flooding processes from produced water composition – a case study from the Halfdan chalk oil field, Danish North Sea. 79th EAGE Conference Exhibition, 1-5 (2017)
- Niels H. Schovsbo, <u>Sofie N. Gottfredsen</u>, Karen G. Schmidt and Thomas M. Jørgensen. *Oil production monitoring and optimization from produced water analytics; a case study from the Halfdan chalk oil field, Danish North Sea*. IFAC-Papers On Line 51 8, 23-210 (2018)

Manuscript in draft, not included in the thesis:

6. Sofie N. Bergfors, Anh K. H. Ho, Annette E. Jensen and Jonas F. Sundberg. *Nontarget screening of dissolved organics in offshore produced water*. To be submitted to PeerJ. The study is not yet approved for publication.

It is noted that the author of this PhD thesis changed name in April 2020. The previous name was Sofie Nitsche Gottfredsen.

## List of Abbreviations

AAD	Absolut Average Deviation
AP	Alkylated Phenols
CID	Charge Injection Device
clr	centered logratio
EM	End-member
DCM	Dichloro Methane
DHRTC	Danish Hydrocarbon Research and Technology Centre
DNS	DHRTC New Samples
FW	Formation Water
GCxGC	Gas chromatography x gas chromatography (2D)
HC	Hydrocarbons
HMI	High Matrix Introduction
HRMS	High Resolution Mass Spectrometry
IC	Ion Chromatography
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
IS	Internal standard
ISO	International Organization for Standardization
LOD	Limit of Detection
LLE	Liquid-liquid extraction
mD	milli Darcy, unit of permeability
mg/L	milligram per liter
m/z	mass-to-charge
OHD	Operator Historical Data
OHS	Operator Historical Samples
OND	Operator New Data
ONS	Operator New Samples
PAH	Polyaromatic hydrocarbons
PC	Principal Component
PCA	Principal Component Analysis
PEG	Polyethyleneglycol
POP-window	Purges Optical Path window
ppb	parts per billion = $\mu$ g/L
ppm	parts per million = mg/L
ppt	parts per trillion = ng/L
PTFE(-filter)	Polytetrafluoroethylene-filter
PW	Produced water
PWC	Produced water chemistry
std.dev.	Standard deviation
SW	Seawater
TDS	Total Dissolved Salt
QTOF	Quadropole time-of-flight
QC	Quality control
1D	First dimension
2D	Second dimension

### List of symbols

- A Absorbance
- Ar (g) Argon, gaseous phase
- c Speed of light
- *c*<sup>\*</sup> Concentration
- °C Degrees celcius
- *E* Energy (of photon)
- E' Emission
- $\epsilon$  Molar extinction coefficient
- *h* Planck's constant
- *I*<sub>0</sub> Intensity of incident light
- *I* Intensity of transmitted light
- kPa kilopascal. Unit of pressure. 100 kPa = 1 bar
- *l* Travelled distance of light
- $\lambda$  Wavelength (of photon)
- Nm<sup>3</sup> Normal cubic metre. Unit of measurement used for natural gas in a reference state of 0°C and 101.325 kPa).
- m<sup>3</sup> (st) Standard cubic metre. Unit of measurement used for natural gas and crude oil in a reference state of 15°C and 101.325 kPa.
- $Mm^3$  Mega ( $M^6$ ) cubic metre

(s) Solid state

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## **1** Introduction

### 1.1 Setting the scene

The global oil demand is increasing, meanwhile, the oil reservoirs are declining, both globally and in Denmark, as shown in Figure 1.1. The decline in oil production puts an increasing pressure on the energy reserved and operators, which are now in the process of finding new ways to produce the remaining oil in place and/or reduce the costs involved with the oil production. A first step on this path is the characterization of the components present in the reservoirs: Oil, gas, water and rock. This work focuses on the water phase. A prerequisite of this PhD work is that all data and samples included are received from TOTAL (Mærsk Oil and Gas until 2018).

This work presents a new, validated, analytical workflow for the analysis of inorganic ions in produced water from oil reservoirs. This is supported by a study of historical produced water chemistry (PWC) data. [96] Overall, the work adds to scale and corrosion prediction and mitigation strategies, and production strategies, for example by supporting simulations, computational modelling and core flooding experiments, and by adding to the understanding of subsurface flow patterns. [78, 95] Additionally, studies of the heavy metals and the organic compounds present in the produced water have been conducted. These contribute to the understanding of the full compositional picture of the produced water and potentially informs future decisions on produced water treatment.



**Figure 1.1:** Oil and water production from the Dan, Halfdan, Valdemar and Kraka fields from 2007 to 2014. The information is from the Danish Energy Agency. [16]

This project is focused on produced water from the Danish North Sea. More specifically, the four fields Dan, Halfdan, Kraka and Valdemar are included in this project. The four fields were chosen because they are currently either water flooded by seawater or are at a production stage where enhanced recovery mechanisms could be considered. For the Dan and Halfdan fields, where water flooding is already employed, the production may be increased by further modifying the composition of the injected water. The Kraka and Valdemar fields are not currently water flooded. The operator has an interest in knowing the potential for the implementation of such a production strategy at the Kraka field. The Valdemar field is a very low permeable reservoir, consequently, making the field a stronger candidate for gas injection. To fully explore the potential, the conditions of the fields must be known in further details – among other things, the geochemistry of the water present must be classified.

The composition of the produced water is important information for the choice of production strategy, especially for the water flooded wells, where an optimized composition of the injection water can contribute to an enhanced production. [84, 102, 109, 110] Additionally, the composition of the produced water may be used to identify wells at which scale formation is a realistic and serious risk. This risk may be reduced by wisely modifying the injected water.

Furthermore, an increasing interest exists in the characterisation of produced water to inform the choice of discharge strategy. Currently, three options for the discharge of produced water are present: Disposal directly to sea, disposal to a waste-well and reinjection into the injection wells. The latter technique demands that the composition of the produced water (which becomes the injection water) is known in details to fully evaluate on the potential for production, and to predict - and preferable avoid - potential risks that may be brought along. These potential risks include loss of injectivity, skin formation and irreversible reservoir damage caused by particles. Currently, in the included four fields, the produced water is discharged back into sea; as the technique for re-injection is not developed. Prior to disposal back into to sea, the produced water is cleaned to avoid that the surrounding marine environment is not harmed. A full characterisation of the produced water provides information for potential improvement of the applied cleaning strategies.

What greatly underlines the importance of the produced water characterisation is the enormous volumes of water that is produced daily, and worldwide. Table 1.1 list the produced oil and water from 1972 (start of production) up to and including 2014 for the four included field. The information is from the Danish Energy Agency. [16] The data from 2007 to 2014 is also plotted in Figure 1.1. Furthermore, the injected water and the calculated water cut [water cut = water produced / (water produced + oil produced)] are given in Table 1.1. From Table 1.1 and Figure 1.1, it is seen that the volume of water produced increases though the life of a well; whereas the oil production decreases. This highlights the need to deal with the big question "what to do with the produced water?". From the four fields included in this study, the water produced in 2014 alone is 22,155 Mm<sup>3</sup>. This is enormous volumes to handle, thus, knowing the composition is crucial for ie. development of cleaning procedures.

			Ō	l producti	on, thous	and cubic	metres			
	1972-2006*	2007	2008	2009	2010	2011	2012	2013	2014	Total
Dan	86,349	4,650	4,241	3,549	2,979	2,474	2,260	2,045	1,794	110,341
Halfdan	29,608	5,785	5,326	5,465	5,119	4,905	4,617	4,150	3,674	68,650
Kraka	4,602	176	112	37	67	170	129	101	89	5,483
Valdemar	3,454	881	1,268	1,410	606	817	844	777	762	11,122
			Wat		tion thou	duo pues	ir metres			
	1972-2006*	2007	2008	2009	2010	2011	2012	2013	2014	Total
Dan	69,190	12,152	13,946	12,889	12,111	10,059	10,468	11,207	14,494	164,515
Halfdan	10,149	4,086	4,766	4,814	5,519	6,149	6,139	6,099	6,574	5,4295
Kraka	4,209	359	436	183	166	358	237	170	214	6,332
Valdemar	3,079	854	925	812	1,207	1,026	893	916	873	10,583
					:	-				
			Š	ater inject	ed, thous	and cubic	: metres			
	1972-2006*	2007	2008	2009	2010	2011	2012	2013	2014	Total
Dan	187,878	20,230	19,275	16,712	15,148	14,508	11,684	10,148	11,568	307,153
Halfdan	34,905	12,727	11,485	11,485	11,945	12,277	10,912	10,921	11,403	128,683
						1				
		>	vater cut	volume v	vater / (vo	lume wat	er + volun	[(IIO 9L		
	1972-2006**	2007	2008	2009	2010	2011	2012	2013	2014	Average
Dan	0.44	0.72	0.77	0.78	0.80	0.80	0.82	0.85	0.89	09.0
Halfdan	0.26	0.41	0.47	0.47	0.52	0.56	0.57	09.0	0.64	0.44
Kraka	0.48	0.67	0.80	0.83	0.71	0.68	0.65	0.63	0.71	0.54
Valdemar	0.47	0.49	0.42	0.37	0.57	0.56	0.51	0.54	0.53	0.49

**Table 1.1:** Volumes of water and oil produced and water injected at the Dan, Halfdan, Kraka and Valdemar fields. The data is from 1972 to 2014 and is from the Danish Energy Agency. [16] From the volumes, the water cut is calculated. All volumes are given in mega cubic metres (Mm<sup>3</sup>) and the water cut is unitless. \*Sum of all the years. \*\*Average of the included years.

## 1.2 Geological settings

The oil province in the Danish North Sea is part of the prolific Central Graben petroleum system in the North Sea distributed between Norway, Denmark, Germany, The Netherlands and the United Kingdom, see Figure 1.2. The Graben was formed as a results of lifting in the Jurassic, followed by subsidence, which resulted in the deposition of the km-thick Jurassic source rock. [34] The primary oil source is the marine Upper Jurassic Farsund Formation. [36] The main oil resource is trapped in Cretaceous-Paleogene chalk which is composed of the remains of calcareous microorganism shells, see Figure 1.3. [46, 66] The generation of oil mainly occurred in the Tail-End Graben and in the northern part of the Saltdome Province, shown in Figure 1.2. [60] This oil was mainly expelled in the Paleocene-Eocene, and, generally, it is recognized that the main filling of the fields is caused by long distance migration of oil from North to the South. [34, 56, 101] The pore pressure in the Chalk reservoirs is strongly overpressured, with a center in the Southern part of the Norwegian Central Graben, see Figure 1.2. From here, the pressure decreases going South into the Central Graben in The Danish North Sea with approximately 55 kPa/km. The pressure gradient causes a water flow velocity within the chalks of, estimated, 2 km/Ma. [56]



Figure 1.2: Map of the Danish North Sea.



Figure 1.3: Stratigraphic overview of the Danish North Sea. The main reservoir ages of the four Chalk fields included in this study (Dan, Halfdan, Kraka and Valdemar) are indicated.

Four fields located in the Danish North Sea are included in this project: The Halfdan, Dan, Kraka and Valdemar fields, see Figure 1.2. A short summary of the fields is given in Table 1.2 and a stratigraphic overview is given in Figure 1.3. A more detailed description of the included fields can be found in the included Paper A.1. [96] In brief, the Valdemar field is distinctively different from the remaining fields, as it produced from a much deeper formation. The Valdemar field is divided into two; North Jens (located North) and Bo (located South). Lastly, the Dan and Halfdan fields are the only water flooded reservoirs.

Parameter	Halfdan	Dan	Kraka	Valdemar
Discovery	1999 [15]	1971	1966	North Jens: 1985, Bo: 1977
In production	1999 [15]	1972	1991	North Jens: 1993, Bo: 2007
Estimated oil in place	1500 MMB. [28]		200 MMB	
Production method	Fracture Aligned Sweep	Water flooded		
	Technology (FAST)	since 1989.		
	concept. [15]			
	Water flooded			
Wells, oil producing	38	61	80	21
Well, injecting	27		0	0
Reservoir formations	Upper Cretaceous	Upper Cretaceous	Fractured Paleogene	Upper Cretaceous Chalk,
	Tor Formation	Tor Formation and	Ekofisk Formation	Lower Cretaceous Tuxen
		the Paleogene Ekofisk		and Sola Formations.
		Formations		High clay content.
Permeabilities	0.5-2.0 mD [28]	0.5 - 2 mD	1-3 mD, effectively	pprox 0.1 mD: Lowest of the
			8 mD. [15, 28]	North Sea chalk field.
Porosities	25-35% [28]		30% [15, 28]	
Other	Also produces gas.	Also produces gas.		Also produces gas.
	The field is developed	The field is divided		The field is divided
	in an alternating pattern	into two major blocks		into two sections:
	of km-long multistage	divided by a major		North Jens and Bo.
	horizontal wells.	fault.		

**Table 1.2:** Overview of the geology of the four fields included in this study: The Halfdan, Dan, Kraka and Valdemar fields.

### 1.3 Oil production

Generally, chalk reservoirs are not as straightforward to produce from as sandstone reservoirs or other carbonate reservoir types. This is caused by a great diversity of grain sizes and shapes in most carbonate sediments. [70] The chalk reservoirs found in the North Sea are also difficult to produce from because of low permeability. Consequently, water flooding has been introduced to some fields as production method. This helps maintaining the reservoir pressure above the bubble point pressure, which improves the physical sweep. [8, 31] As seawater is easily available at off-shore platforms, this is often the injection fluid of choice. Studies suggest that seawater increases the oil recovery by spontaneous imbibition and viscous displacement. [102] Furthermore, studies show that the injection of seawater into a carbonate (chalk) reservoir can affect the wettability of the rock positively towards a more water-wet nature. [8, 84, 102, 109, 110] The mechanism behind this effect is not fully understood. By nature, pure chalk is water wet, but in most reservoirs mixed-wet behaviour is observed. This is most likely caused by a layer of material on the carbonate (chalk) surface. Thus, to improve the oil production further, this layer must be modified which may be done through the injected water. Some studies suggest that the adhesion of polar organic molecules to the rock is affected by changes in the total concentrations and the concentration ratios between divalent ions (with emphasis on  $Mg^{2+}$ and  $Ca^{2+}$ ). [8, 18, 109, 110] Also, the injected fluid (water) may affect the compaction of the reservoir. [18, 102, 109] In the cited studies, low-salinity water flooding has shown great potential in carbonate reservoirs. [4, 13, 14, 35, 71, 93, 114] Other studies disagree, thus, the actual potential is not clear presently. [7, 10, 29]

In the Danish North Sea, seawater is used as the injection water fluid. Prior to injection, the water is treated to limit the risk of accumulation of sulphate scales, and for some fields to improve the recovery. To limit sulphate scale accumulation, the seawater is filtered and  $O_2$  is removed. [42] Methods to improve the oil recovery include low-salinity water flooding, surfactant flooding, gas injection and Smart water flooding. [6, 13, 14, 73] None of these techniques are employed at any of the fields included in this study.

In short, the composition of the reservoir fluid is key for the production of oil and to improve production further, the composition of the injected fluid (seawater) may be adjusted. A first step to determine the optimal composition of the injection fluid is to characterise the present fluids; historically and current.

Chemically tweaking of the reservoir fluids is not the only applied production strategy. For example, horizontal wells (commonly 2 km in length) are used to develop chalk fields. [72] This is implemented on the Halfdan field, which is developed very systematically. [15] At the Halfdan field, acid stimulation upon completion was implemented to enhance productivity. [19] Overall, physical and chemical alternation of the reservoir is potentially a powerful combination for an optimal production.

The injection of new fluid (water) into the reservoir introduces risks. Common consequences for water flooding include increased scale and corrosion. Scale is a documented problem at for example the Halfdan field. [107] In Danish chalk fields, the most critical scale types includes the hard, insoluble scales  $BaSO_4$  and  $SrSO_4$ . But also the soft scales such as iron scales (ie.  $Fe(OH)_2$  and  $Fe(OH)_3$ ) and  $CaCO_3$  have been identified. [39, 63, 97, 98, 109] Due to the high amount of  $SO_4^{2-}$  introduced with the injected (sea)water, water flooded reservoirs are especially vulnerable. Prediction of scale formation is solidly founded on the concentrations of ions measured in the water at the wellhead.

### 1.4 History of produced water

Before the 20th century, petroleum was mainly used as a medicine, lubricant and waterproofing agent, as well as a source for light and heat. Most petroleum was, at that time, found as a bi-product when settlers were digging wells in a need for acquiring salt. No one questioned the co-existence of the saline water and the oil. It was not until 1938, the existence of saline interstitial water in oil reservoirs was recognized. [5, 92] It was believed that there was a definite separation of water and oil in the reservoirs and that mixing of the two did not take place until the reservoirs were tapped. In 1928, the first commercial laboratory for the analysis of rock cores was established by Torrey (Pennsylvania, USA). Core extracts were tested, leading to the suspicion that "water was indigenous to the oil productive sand". [5] This was later recognized. [79] Beginning in 1920, the impact from the water on the movement of oil was started to be studied. Munn proposed that the movement of underground water might be the primary cause for the migration and accumulation of hydrocarbons (oil and gas). [67] In 1923, Rich postulated that water was an integral part of the oil and that the two could move jointly independently on the speed of the movement. Today, it is commonly recognized that water significantly affects the displacement of oil during production and that water plays a central role in the production of oil and gas.

At the present day, the origin of formation water is still being discussed. Two strong hypotheses are prevalent. [51] Some scientists suggest the chemical composition of basinal brines reflects the conditions at the time the waters were formed; while others argue, the composition of the waters are determined by late-stage diagenesis. Hanor and McIntosh have studied basinal brines in the Gulf of Mexico and argue that the Na<sup>+</sup>-Mg<sup>2+</sup>-Ca<sup>2+</sup>-Cl<sup>-</sup> composition of the brines are product of diagenesis. The exact reactions are not known for sure but may include dolomitization (depletion of Mg<sup>2+</sup>) and albitization of Ca<sup>2+</sup>-plagiocalse (enrichment of Ca<sup>2+</sup> and depletion of Na<sup>+</sup>). One certainly important diagenetic reaction includes the dissolution of salt (NaCl), which provides the continuing source of Cl<sup>-</sup>. [51] This is also argued as being the source for the high-saline formation water observed in the North Sea as presented later in this work. [96]

### 1.5 Chemistry of produced water

The water originally present in reservoirs, prior to any production, is called formation water. For non-flooded reservoirs, this is the only water being produced. For water injected reservoirs, the formation water is only produced at the beginning of the production; up til 1-5 years after injection of water has been employed. After injection water breakthrough, a mixture of the formation water and the injected water (often modified seawater) is produced. It is expected that the produced water will gradually change from having a formation water compositional characteristic, to a solely injection water characteristic; similar to seawater characteristics.

One of the major differences between formation water and seawater, is the salinity. Despite the fact that the salinity of formation water varies (also within the North Sea fields), it typically has a salinity that is two to three times higher than the salinity of seawater. [109, 86] Furthermore, the  $SO_4^{2-}$  concentration differs significantly; it is three to six times higher in seawater than in formation water. Historically, the  $\mathrm{SO}_4^{2-}$  concentration has been used as marker for injection water breakthrough. The CI- concentration has routinely been used to study flow pattern of the formation water. Unfortunately, less attention has commercially been paid to the remaining inorganic ions. This is a pity, as they also contain a wealth of information: K<sup>+</sup> may be used a tracer for the clean-up ability of a well. It is often introduced to the reservoir in levels significantly higher than the natural level with drilling muds, that are used in the very initial phase of a well's life. [88] The natural concentration is highly determined by the release from clay minerals in the reservoir.  $Ca^{2+}$  and  $Mg^{2+}$ can be indicators of dissolution and adsorption on the surface of the rock, thus, conveying valuable information on recovery mechanisms. [8, 84, 86, 109] This is information that is especially relevant when trying to understand and enhance the production via (modified) water injection. Last,  $Sr^{2+}$  and  $Ba^{2+}$  are highlighted as important ions. They are the contributing factors to scale formation, which is especially problematic at the Halfdan field (in the list of the included fields). Figure 1.4 shows a map of the Halfdan field, in which the wells where significant scale is observed are marked. The observed hard scales include SrSO<sub>4</sub> and BaSO<sub>4</sub>. These are especially critical when formed in the deep wells at the Halfdan fields as these cannot be reached with the commercially available tools. A worst-case consequence of this is a partial closure of section of the relevant wells. Sulphate scale formation becomes especially relevant in water flooded wells, as the injected (sea)water introduces high amounts of  $SO_4^{2-}$ . For an accurate and sensitive prediction of the scale formation risk, the concentration of SO<sub>4</sub><sup>2-</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> must be known accurately.



**Figure 1.4:** Map of the wells in the Halfdan field. Wells where scale has been observed are marked with a yellow star. The original picture is from the Danish Energy Agency. [15] Information on scale observation has been added by the author based on information from the field operator.

Produced water contains traces of both heavy metals and organic compounds in addition to the mentioned ionorganic ions. [25, 49, 103] The organic components most likely originate from the petroleum that the formation water is in direct contact with inside the reservoirs. Heavy metals may be of natural origin, but may also be introduced to the reservoir through tubing, completion chemicals and production chemicals. [25] Recently, more focus has been brought to these low-concentrated constituents in the produced water. [103] Currently, the regulations for discharge water is set in the OSPAR convention from 1998. [76] This sets a limit of 40 mg/L dispersed oil in water as an annual average. What is less studied is the organics dissolved in water. Most documented studies on the dissolved organic compounds cover small organic acids. [65, 106, 115] Also, naphthenic acids have been studied extensively. [99] Generally, the level of dissolved organic acids is low in North Sea waters. [104, 105] For a full evaluation of the organic content, more organic components must be included in the evaluation. The work presented in this thesis provides important input for e.g. the decision making on discharge strategies. Presently, these strategies include disposal directly to sea, disposal to a waste-well and re-injection. Regardless of the disposal strategy, a complete characterisation of the produced water supports the following determination of how the water is treated prior to discharge.

In order to know the composition of produced water, heavy metals, even in trace amounts, are important to include. [25, 91, 111] A published study of produced water from Brazil reports observations of heavy metals in the produced water in significant concentrations. [111] This proves that heavy metals are present in the produced water, and that the concentrations of these must be monitored to know the full composition of the produced water.

Most existing reported techniques for the analysis of trace metals in (highly saline) produced water samples are mono-elementary and/or include laborious pre-treatment of the samples. [9, 25, 26, 27, 37, 61, 62, 89, 91, 116] Only few studies present multi-elementary techniques with little sample pre-treatment, as the technique presented in the present study. [111] This is advantageous especially if the analysis of trace metals has to be done routinely. Most of the existing studies on heavy metals in produced water has been conducted in Brazil. And, to the knowledge of the author, no publications on metals in the Danish North Sea exist, thus, this work is an important contribution to this evolving field.

### 1.6 Introduction to methods

Historically in Denmark, off-shore produced water samples have typically been analyzed with respect to inorganic ion content using ion chromatgraphy (IC) - and early analyses also include titration. This technique is adequate for the analysis of inorganic ions present in concentrations above 1 mg/L, which include Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> - but not always Ba<sup>2+</sup>. For many PW samples, the Ba<sup>2+</sup> concentration is significantly below 1 mg/L. Previously, the concentration of Ba<sup>2+</sup> in such samples have been reported as "not detected". For the improved modelling and prediction of scales, the Ba<sup>2+</sup> concentration is crucial to know; even when it is very low. Thus, a more sensitive technique for the analysis of Ba<sup>2+</sup> is desirable for the industry. The remaining ions are not excluded from the benefit of these improvements as small changes may be interesting to follow. For the analysis of the inorganic cations, we introduce Inductively Coupled Plasma - Optical Emissions Spectroscopy (ICP-OES).

Inductively coupled plasma (ICP)-based analytical techniques have been used routinely in regulated water analysis since the early 1980s. [82] These cover ICP-optical emission spectroscopy (ICP-OES) and ICP-mass spectrometry (ICP-MS). The combination of low detection limits (<1 ppm) and wide analytical linear range (emission wavelengths: 170 nm to 800 nm for ICP-OES) makes the techniques particularly well suited for the analysis of the many elements of interest present in low to moderate concentrations in produced water samples. Additionally, the ICP-based techniques have the ability of simultaneous multi-element determinations. Generally, an ICP-based technique can handle the measurement of up to 30 elements in one sample. Furthermore, the techniques can operate with high-matrix samples (up to 30% TDS). Both are capabilities that are crucial for the samples discussed in this project. On top of this, due to the multi-element analysis, these techniques are significantly faster than the ones previously used. Once the instrument is running, ICP-OES requires approximately ten times less operation time than common IC.

One major drawback of ICP-OES is that it analyzes only elements (not molecules), therefore, ICP-OES must be combined with other analytical techniques to cover all analytes of interest in the PW samples. Here, we combine ICP-OES for the analysis of the cations, with IC for the analysis of anions, which are present in concentrations well above 1 mg/L. An IC can, indeed, analyse both cations and anions, but a change of column and eluent is required. Thus, independently of the analytical method chosen (full IC or ICP-OES combined with IC), the analysis of cations and anions must be done separately. The concentration of the anions (CI<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) in our samples are at >100 mg/L level, whereas  $Ba^{2+}$  reaches <1 mg/L levels, thus, making the combination of ICP-OES (for cations) and IC (for anions) extremely powerful for the analysis of the produced water (and alike) samples.

Data on the produced water chemistry has been analysed with Principal Component Analysis (PCA). PCA has the ability to find both trends and outliers in large data sets, thus making it a good fit for the need.

ScaleCERE is a program based on the Extended UNIQUAC model, which perform thermodynamic calculations on fluids based on their ionic compositions and physical conditions. [59, 113]. The program is used as a tool for the prediction of potential scale formation. ICP-MS is introduced for the analysis of heavy metals in the produced water samples. Information from the analyses will add to a geochemical study. ICP-MS has a lower limit of detection than ICP-OES, which is needed for the analysis of heavy metals as these are expected to be present in ppb-level (as oppose to ppm-level for the remaining inorganic ions previously mentioned).

For an even more detailed classification of the water, a study of the organic content of the PW samples are included in this project. Organic acids are more soluble than other constituents of the crude oil due to their high polarity. Therefore, these are expected to be the organic compounds present in the highest concentrations in the produced water. [1] Also, smaller alcohols, acids and PAH's are expected to be present in the samples. [65, 99] Organic acids in reservoir waters are most typically present in concentrations of around 0.2-2.0 mM, thus sensitive analytical techniques are required. Moreover, the most dominant acids present are the short chain aliphatic carboxylic acids (1-5 carbons) and acetic acid, thus a method targeting small organic compounds is preferred for this purpose. [65, 105, 106] In the present project, two-dimensional gas chromatography (GCxGC) coupled with a high-resolution mass-spectrometer (HRMS) was used for the analysis of the organic content in the produced water samples. Using 2D chromatography is needed to resolve the complexity of these samples.

### **1.7** Motivation and research questions

One of the potentially most promising enhanced oil recovery (EOR) approaches in the Danish North Sea is chemical alteration of the injection water. [4, 8, 14, 93] Water based EOR covers different techniques, for example low-salinity flooding (often seawater is injected) and SmartWater flooding, to optimize the flow of oil and to minimize the residual oil left behind. [8, 14] Both methods introduce a new liquid to the reservoir, which can have consequences. Precipitation of sulphate-scales is a commonly known consequence, which shortens the lifetime of a well. Moreover, corrosion is a factor that impacts a well's lifetime. A characterization of the water present in the reservoirs is crucial to minimize the risk of scale and corrosion, extend well lifetime, and to optimize the oil production.

Commonly, the off-shore produced water is discharged to sea which is accompanied by restrictions set by legislation. [49, 76] Currently, the potential for re-injection of the produced water is being investigated. Independent of the future fate of the produced water, its compositions must be known in details. This includes inorganic ions, as well as the more toxic heavy metals and organic compounds. All in all, a thorough examination of the reservoir water is required for proper decision making.

The specific aims of the present project are:

- Develop a fast and sensitive analytical workflow for inorganic ions in produced water.
- Classify water types in the Danish North Sea to input for targeted modelling, simulations and core-flooding experiments.
- Characterize the water types in the reservoirs to identify geochemical trends and predict the risk of scale formation.
- Evaluate the regional dependency on the potential for water flooding.
- Characterize the produced water with respect to heavy metals and organic compounds for further input to the characterisation of the produced water types across the fields.

To restrict the present study, focus has mainly been on the Halfdan field. This implies to the studies on heavy metals and organic compounds, where more expensive analytical methods have been applied.

### 1.8 Layout of thesis

This PhD thesis includes 9 chapters, which covers the theoretical and practical aspects of the work behind the experimental analysis of the produced water samples, and the following handling and discussions of the output data on the produced water chemistry. The main content of the different chapters is as given below.

**Chapter 1** gives an introduction to the framework in which this PhD is conducted. It provides background information on produced water and its chemistry. Also, it outlines the motivation and goals of this thesis.

**Chapter 2** introduces the historical produced water chemistry (PWC) data that is part of the foundation for this thesis together with the computational methods that have been used to analyse this data. These include Principal Component Analysis (PCA) and thermodynamic modelling using the Extended UNIQUAC software.

**Chapter 3** contains a detailed description of the experimental techniques that have been employed in this project. These cover ICP-OES, ICP-MS, IC and GCxGC-HRMS. The sampling of off-shore produced water samples is not straightforward and will be discussed here.

**Chapter 4** presents and discusses the main findings from the analysis of historical PWC data from the Dan, Halfdan, Kraka and Valdemar fields in the Danish North Sea. Temporal and regional variations in the PWC are discussed and five end-member water types are classified. The hydrodynamic information extracted from the water types is presented and the application of the water types in relation to production and scale mitigation strategies is discussed.

**Chapter 5** describes a new, sensitive and fast analytical technique for the analysis of off-shore produced water samples from the Danish North Sea using ICP-OES combined with IC. The technique is applied to produced samples from the Halfdan field and the analytical results here from are presented and discussed. Especially novel is the increased sensitivity for the analysis of  $Ba^{2+}$  in the samples, which provides valuable input to scale and corrosion mitigation strategies.

**Chapter 6** presents an evaluation of observed compositional changes in the produced water samples that have taken place during storage for one year. The findings reveal the value of long-time stored samples and their potential use in further analysis.

**Chapter 7** focuses on the analysis of heavy metals in off-shore produced water samples from the Halfdan field. ICP-MS in HMI mode was used for the analysis, which is still under development. The preliminary findings are presented and the work going forward is discussed.

**Chapter 8** presents the experimental work going into the non-target screening of organic compounds in off-shore produced water samples from the Halfdan field using GCxGC-HRMS. The organic compounds may be used for further characterisation of water types.

**Chapter 9** collects the above chapters and wraps up the main findings. In this chapter, the application of the findings will be discussed in depth and direct recommendations for taking this work further will be given.

**Chapter 10** briefly describes additional contributions of the PhD study presented in this thesis.

Chapters 4, 5 and 6 are based on papers, some of which are drafts not yet accepted. They give a short introduction to the study and point out the core findings. The detailed studies are presented in the papers found in the Appendix.

## 2 Data and methods

### 2.1 Data

Data from produced water analysis of four fields in the Danish North Sea (Halfdan, Dan, Kraka and Valdemar) has been included in this study. The produced water chemistry (PWC) data has been received from the operator (Mærsk Oil and Gas at that time) upon request. Samples have continuously been collected and analyzed by the operator, primarily with the goal of monitoring the breakthrough of injection water (total salinity,  $CI^-$  and  $SO_4^{2-}$ ) and the chemical injection performance and scale potential ( $Sr^{2+}$  and  $Ba^{2+}$ ).

The data from the operator covers analyses of the ionic composition of produced water samples and includes, for the majority of the samples, all the concentration measurements of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> - and for a few samples also Br<sup>-</sup>. Additionally, the well and sampling date has been given. For some samples the time of day and the sampling personnel is provided. The data covers measurements from the very early stage of production (Dan: 1972; Halfdan: 1999; Kraka: 1991; Valdemar, North Jens: 1993, Bo: 2007) and up to and including 2015. In total, the data set is named Operator Historical Data, abbreviated OHD, and covers 8,749 samples distributed over 161 wells. The samples are distributed as follows:

- Halfdan: 40 wells, 3,668 samples.
- Dan: 88 wells, 4,895 samples.
- Kraka: 7 wells, 71 samples.
- Valdemar: 26 wells, 140 samples.

For Halfdan, PWC data up to and including 2019 is included. This is also from the operator and is provided upon request, because it allows for a comparison of the results from the in-house analysis of recent samples from Halfdan (Section 3.1). This data set is named Operator New Data (OND) and includes 1,185 samples (dating 2016-2019) covering 42 wells on Halfdan.

All data from the operator stems from analysis of produced water samples; collected and analyzed by the operator. The water samples have been collected at the test separator at the off-shore platforms. In the test separator, water, oil and gas are separated based on gravity, similar to the separation in the production separator. Fluids from several wells are collected from the same test separator. To ensure a representative sample, the well of interest is on test for at least 12 hours prior to sampling. At this time, all fluids from the previous well are expected to be displaced. Furthermore, good flushing through the sampling pipe for a few minutes must be ensured before the final sample is collected. The water samples are collected on average at quarterly intervals from each well. Immediately after sampling, acid (HCl and/or HNO<sub>3</sub>) has been added to the produced water (unless else is told), in order to prevent bacterial activity and limit the risk of solid precipitation in the samples. The samples have then been transported on-shore (arrival in Esbjerg, Denmark) for analysis in the laboratories (located in København, Denmark). The analyses at the operator have primarily been carried out by ion chromatography, and some early

analyses include titration. Further details and the precise procedure is unknown to us.

### 2.2 Principal Component Analysis (PCA)

Principal component analysis, PCA, is used to study the PWC. It is a multivariate data analysis method often used to reveal hidden data structure; trends and outliers. [17] PCA was first formulated in 1901 by K. Pearson. He formulated the analysis as finding "lines and planes of closest fit to systems of points in space". [58] PCA was introduced in chemistry by Malinowski around 1960. Here it was named principal factor analysis. [30, 100] After 1970, many chemical applications of PCA have been published. [30] In this project, PCA is used to localize trends and patterns in the PWC data.

PCA estimates the correlation structure of the variables by the use of orthogonal transformation. A set of observations of possibly correlated variables, here ion concentrations, are converted into a set of linearly uncorrelated variables. These are called the principal components (PC). The first principal component (PC-1) lies along the direction of the maximum longitudinal variance in the data set. The second PC (PC-2) lies along the direction of the second largest variance - orthogonal to PC-1. PC-3 lies along the third largest variance, orthogonal to both PC-1 and PC-2, and so forth. [52] The PCA is performed with The Unscrambler X 10.5.1 software package by Camo Analytics. [17, 20]

### 2.2.1 Normalisation of data

Compositional data, such as that used in this work, is mathematically presented as points on a simplex. Each point is a quantitative description of a subset of some whole, thus, each point contains relative information. To normalise the data, it has been centered logratio (clr) transformed. This transformation is often applied to geochemical data, and is considered as the generally accepted standard, particularly for compositional data. [44, 45, 55, 80, 81, 87] A more detailed description of the data preparation, going forward of the PCA, is described in the attached Paper A.1. [96]

### 2.3 Thermodynamic modelling

Thermodynamic modelling is used to predict the potential for the formation of carbonate and sulphate solid formation (the scale potential) of different produced waters. [11, 12] The Extended UNIQUAC (universal quasichemical) software is a thermodynamic model designed for electrolyte solutions and is used for this purpose. The model can be used to calculate thermodynamic properties and phase equilibria of solid-liquid, liquid-liquid and gas-liquid systems. It is described in detail by K. Thomsen. [32, 59, 113] The Extended UNIQUAC model performs general phase equilibrium calculations for aqueous solutions with the ions Na<sup>+</sup>, H<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup>, Cl<sup>-</sup>, OH<sup>-</sup>, SO<sup>2-</sup><sub>4</sub>, HSO<sup>-</sup><sub>4</sub>, CO<sup>-</sup><sub>3</sub>, HCO<sup>-</sup><sub>3</sub> under the given pressure and temperature conditions. K<sup>+</sup> is included as Na<sup>+</sup>, as these two elements have similar thermodynamic properties. The model outputs the saturation index (ionic activity product divided by the solubility product, abbreviated SI) of relevant minerals in a solution. At saturation, the SI is equal to one and at a saturation index higher than one the solution is supersaturated and minerals may precipitate. The amount of expected solid formed is calculated by the software. Extended UNIQUAC only includes thermodynamic in its calculations, but other factors also affect the actual scaling potential. These include kinetics, flow patterns in the wells, sticking factor for a given solid to the surface and the nature of the surface of the well tubing. However, the first prerequisite for scale formation is a state of supersaturation, thus, the results from the Extended UNIQUAC calculates provides indications for the potential of scale formation. The concentrations of key ions are the main denominator for the scale potential, and is known to vary from well to well. Therefore, the risk of scale formation needs to be evaluated for each individual well.

The data provided does not include information on the temperature, pressure,  $HCO_3^-$  concentration and pH typical for each sample. Consequently, assumptions of these values must be made to allow for the calculations. How this is done is described in details in "Paper 1", see Appendix A.1. [96]
# 3 Experimental techniques and samples

The objectives of this thesis all relate to the chemical composition of produced water and the information to be extracted from it. To study these compositions, samples are needed as well as the application of several analytical techniques. The ionic composition of a large number of samples were analyzed with a combination of Inductively Coupled Plasma - Optical Emissions Spectroscopy (ICP-OES) and Ion Chromatography (IC). The heavier inorganic ions (trace metals) were analyzed using Inductively Coupled Plasma - Mass Spectroscopy. Further, the organic compounds dissolved in the water samples were analyzed using two dimensional Gas Chromatography (GCxGC) coupled with highresolution Quadrupole Time-of-Flight Mass Spectrometry (QTOF-MS). The techniques were specifically chosen to achieve complementary information, with the possibility for some inter-instrumental testing of results. Also, the presented techniques provide a high sensitivity, adding to the current information about the type of samples studied in this project.

# 3.1 Produced water samples

The majority of the samples made available and included in this study originate from the Halfdan field. At the Halfdan field, the samples are sampled from one of two production platforms. Picture 3.1 provides an overview of the wells, and the two production platforms at the Halfdan field. Samples from HBA- and HBB-wells are collected at platform HBA and samples from HDA-wells are collected at the HDA platform.



**Figure 3.1:** Map of the Halfdan field from the Danish Energy Agency. [15] The production platforms, where the samples were collected, are highlighted.

Samples from Dan and Kraka are all collected at the Dan F platform. As for Halfdan, the production from the Valdemar field is divided in two. Fluids from the North Jens area are produced at the Valdemar AB platform, and fluids from the Bo area at the Valdemar BA platform. This is illustrated in Figure 3.2.



**Figure 3.2:** Map of the Valdemar field from the Danish Energy Agency. [15] The production platforms, where the samples were collected, are highlighted.

#### 3.1.1 Off-shore samples

This work deals with the chemical analysis of produced water samples from the Danish North Sea. The water is produced as a by-product along with the production of oil and gas at the offshore platforms. The water can either originate from natural water zones in the reservoirs; or a production of the water that may have been injected to the reservoir to enhance the oil production from the reservoir; or a mixture of the two water types. [96] With time, the volume of produced water increases, whereas the volume of produced oil decreases. In 2013, the produced volume of oil was 10.2 Mm<sup>3</sup>, gas 4.7 million Nm<sup>3</sup>, and water 33.3 Mm<sup>3</sup> (as a reference, 35.4 Mm<sup>3</sup> water was injected) in the entire Danish North Sea (all 19 Danish fields included, the four fields included here make up about 50% of the total production). The numbers for the four field included in this study are given in Table 3.1. [15]

	Oil	Gas	Water produced	Water injected
	Mm3	million Nm <sup>3</sup>	Mm <sup>3</sup>	Mm <sup>3</sup>
Dan	2,045	416	11,207	10,148
Halfdan	4,150	1,389	6,099	10,921
Kraka	101	20	170	None
Valdemar	777	368	916	None

Table 3.1: Production in 2013. [15]

The produced oil, water and gas condensate are separated at the production platforms in the test separators. These take advantage of gravity to separate the three phases. Even after separation, the produced water contains residues of oil (dissolved and suspended in the water) and particles (organic and inorganic). Water (and oil) produced from different wells passes the same test separator at different times (hence, they are not directly mixed) which may cause cross-contamination of samples from different wells because residues of one sample is left in the test separator once the next enters. The separator is "flushed" with the new samples for minimum of 12 hours prior to sampling, to limit the risk of cross-contamination.

#### 3.1.2 Historical samples from the operator

Since field production was initiated (Dan: 1972, Halfdan: 1999, Kraka: 1991, Valdemar: 1993), the produced water has been sampled and analysed. Most of the samples have been acidified prior to analysis (HCl and/or  $HNO_3$ ) to conserve the samples. The sampling and sample treatment follows procedures set by the field operator. A selection of the samples are made available to us (given directly to us from the operator's laboratory). These have been sampled from October 2017 to and including June 2018. They were all received in November 2018. In total 163 samples were included. The details of these are given in Table 3.2. These samples are referred to Operator Historical Samples (OHS).

Field	Well area	Number of samples
Dan	MFF	35
Halfdan	Total	99
	HBA	38
	HBB	12
	HDA	49
Kraka	A	7
Valdemar	Total	20
	VAB	10
	VBA	10

**Table 3.2:** Origin of Operator Historical Samples (OHS). These have been sampled with an old sampling protocol, where the details are unknown to us.

#### 3.1.3 New samples collected with documented protocol

In October 2018, a sampling campaign was implemented following a new revised sampling protocol. This imposed a set of restrictions to the off-shore sampling procedure and the following handling of the samples. Thus, limiting the introduction of unknowns and contamination of any kind. The revised procedure included the following requirements:

- The produced water samples (1L) must be sampled at the test separator.
- No chemicals (eg. acid and scale inhibitor) must be added to the produced water samples.
- The produced water samples are stored in 1L oil resistant fluorinated plastic containers.
- The produced water samples are stored at room temperature, in the dark, prior to transport.

The water samples were collected at the test separator, in which water, oil and gas condensate are separated. The separation is based on gravity, similarly as to the separation in the production separation. The difference between the two is that the test separator is smaller in size compared to the production separator and that it has more instrumentation. Fluids from a range of wells is separated in the same test separator, but at different times. To ensure all fluids from the previous well is displaced and, thus, avoiding crosscontamination of samples, the fluid from a well is flushed through the separator for a minimum of 12 hour before a sample from the well is collected. The samples are normally not cleaned further (filtration etc.), before they are transferred to the laboratory.

Once sampled, the produced water is transported on-shore to Esbjerg, Denmark, from where the samples are transported to the DHRTC laboratory (Lyngby, Denmark). The time from sampling to the arrival in our laboratory is about one month. Upon the arrival to the laboratory, the samples were registered, transferred to 1L blue cap bottles and stored in a refrigerator at  $5^{\circ}$ C. The special sampling procedure was used from mid June 2018 to mid March 2019.

The produced water collected with the new sampling protocol include 86 samples distributed over 51 wells; samples from all the included fields have been collected, but the majority of the samples are from the Halfdan field. These are listed in Table 3.3. For all samples through time (all sampling methods), the field, well, sampling point, sampling date and sampling personnel is given. For some samples, the time of sampling is also given. The samples are referred to as DHRTC New Sample (DNS).

Field	Well area	Number of different wells	Number of samples
Halfdan	Total	34	61
	HBA	17	28
	HBB	5	8
	HDA	12	25
Dan	MFF	5	9
Kraka	A	7	7
Valdemar	VBA	5	8

**Table 3.3:** Origin of DNS samples; these have been sampled with a new revised sampling protocol. The procedure is described above the table.

# 3.2 Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES)

Plasma is one of the four common states of matter (solid, liquid, gas, plasma). Like gas, plasma does not have a definite shape or volume. Instead, it is electrically conductive and produces electric currents. This ability arises because, in a plasma, electrons are separated from their positively charged nuclei, forming an "electron sea". Inductively Coupled Plasma (ICP) was developed in the early 1960s and uses this "electron sea" as an ion source. [57] The plasma is formed in a stream of argon flowing through an electromagnetic field. In the ICP, the plasma is formed in the plasma torch, which is described in further detail in Section 3.2.1. A peristaltic pump delivers the aqueous sample into an analytical nebulizer. Here it is converted into a mist, that passes through a spray chamber. In the spray chamber big droplets are removed. Consequently, only small droplets are allowed to pass through the spray chamber to the plasma, where the solvent evaporates off. The sample is introduced directly into the plasma, where it is immediately bombarded with electrons and charged ions. The full set-up of the ICP-OES found in the DHRTC laboratory is shown in Figure 3.3. The different components are described in the following sections.



Figure 3.3: Illustration of the ICP-OES set up.

As a consequence of the bombardment, the sample molecules decompose into their respective atoms. These generated atomic ions are excited and will eventually convert to a lower energy state. A process that causes a photon to be emitted. The energy (which is measured by the wavelength) of this photon is unique to the specific elemental ion, thus, it can be used for identification via emission spectroscopy. Each element emits photons with several characteristic wavelengths, creating an unique emission spectrum. The intensity of the emitted light is correlated to the quantity of the elemental ion (atom) in the sample, allowing for quantitative analysis. ICP instruments coupled to optical emission spectroscopy (OES) has been commercially available for approximately 25 years and is today commonly used for metal and semi-metal analysis. [38, 62, 111]

One of the main advantages of using ICP-OES is its ability to carry out multi-element determination; and the inclusion of both all the metallic and roughly half of the nonmetallic elements in the periodic table. Analytical wavelengths range from 170 nm to 800 nm. Furthermore, an ICP-OES can handle the measurement of up to 30 elements in one sample. However, one must be aware of the risk of spectral interference. Also, a risk of ionization suppression complicates the analysis of high-matrix samples.

#### 3.2.1 Plasma source

In ICP, an argon plasma is the source of energy that excites the atoms, which causes them to emit photons. The plasma is formed by ionizing a flowing stream of argon gas; this produces argon ions and, more importantly, electrons. An argon plasma reaches temperatures of 6,000 - 10,000 K, caused by resistive heating from the movement of the electrons and argon ions in the gas. Due to this extremely high temperature, an argon plasma provides extremely efficient atomization and ensures a high population of the excited states in the atoms - giving a high sensitivity. The temperatures are dependent on the purity of the used gas. The cleaner the gas, the higher the temperatures may be reached.

The argon plasma is formed in the ICP torch, which in this case consists of three concentric quartz tubes, surrounded by a radio-frequency induction coil (at the top). The sample is mixed with a stream of argon gas (carrier gas) and carried to the central capillary tube of the torch. When the sample is flowing, the plasma formation is initiated by a Tesla coil spark. The argon ions and the electrons move in a circular path induced by a fluctuating magnetic field created by an alternating radio-frequency current in the induction coils. As a result, the sample gas (unionized at this time) collide with the argon ions and electrons, giving rise to resistive heating. At the base of the plasma, temperatures may reach 10,000 K. And 15-20 mm above the coil, the temperature is around 6,000 - 8,000 K. This is where the emission (of photons) takes place. To protect the outer (third) quartz tube from these high temperatures, a flow of argon streams to ensure thermal isolation. Figure 3.4 show a schematic set-up of the torch.



**Figure 3.4:** Illustration of the ICP torch. Here the plasma is formed. The picture belongs to Thermo Fischer Scientific. [112] Temperatures have been added by the author.

#### 3.2.2 Optical emission spectroscopy

Spectroscopy is a method of chemical analysis that studies the interaction between electromagnetic radiation and a studied matter. In this project, optical emission spectroscopy is used, which is the study of electromagnetic radiation emitted by atoms. The emission of radiation is caused by energy transitions of outer shell electrons within the studied atoms. Within atoms, the electrons exists in discrete energy levels, named atomic orbitals. The atomic orbitals are quantized, meaning they have defined values. Electrons can move between orbitals, as long as the total energy is conserved. In order to this holds true, the atom may either gain energy by absorbing a photon or release energy by emitting a photon. In emission spectroscopy, atom drops to a lower energy state (often from an exited state), causing them to emit a photon with an energy unique for the identity of the atom. Each element has a unique number of electrons with specific energies, and consequently an atom can emit photons with different, specific, energies creating a unique pattern. The energy of the photon is inversely proportional to the wavelength, given by Equation 3.1.

$$E = \frac{hc}{\lambda} \tag{3.1}$$

Here E is the energy, *h* is Planck's constant (6.62607004×10<sup>-34</sup> m<sup>2</sup> kg s<sup>-1</sup>), *c* is the speed of light and  $\lambda$  is the wavelength of the photon, often given in nm.

The unique set of wavelengths, characteristic for an atom, is called a spectrum. The emission spectre of four of the atoms studied in this project are given in Figure 3.5.



**Figure 3.5:** Emission spectra of Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and Ba<sup>2+</sup>. The spectra are reproduced from Penn State Behrend University. [83]

The identification of atoms is based on the observation of photons emitted from a sample at specific wavelengths. According the theory presented above, emission lines are expected to be sharp. Actual line shapes are disturbed by Doppler, collision and proximity broadening. Consequently, the observed line is actually peak, with the maximum at the wavelengths determined from the energy levels. Observed peaks for the included analytes are shown in Figure B.4. Due to the line broadening, peaks may overlap if they are close in energy. This causes spectral interference. If possible, analytical wavelengths are chosen to avoid spectral interference between the elements in the samples. If not, possible peak deconvolution is the alternative approach.

For quantification of these atoms, the intensity of the light ("number of photons") is used as it is proportional to the concentration of the studied compounds (number of atoms) in the sample. Lambert-Beer's Law, given in equation 3.2, states the relation between the measured intensity and the concentration of the specific atom. [77]

$$A = \log \frac{I_0}{I} = -\log(E') = \epsilon \cdot c' \cdot l \tag{3.2}$$

Here *A* is the absorbance,  $I_0$  is the intensity of the incident light, *I* is the intensity of the transmitted light, E' is the emission,  $\epsilon$  is the molar extinction coefficient (a constant), c' is the concentration of the analyte in the sample, and *l* is the travelled distance of the light.

The emission of photons only takes place if the atom is in an energy excess. To produce this excess energy and create atomic ions, we use an inductively coupled plasma as the source for energy.

#### 3.2.3 The instrument

The instrument used in this study is an iCAP<sup>™</sup> 7200 from Thermo Fischer. It uses an Echelle optical design and a Charge Injection Device (CID) solid-state detector to measure trace elemental concentrations in aqueous solutions. The CID detector is kept cold by thermoelectric cooling with a ThermoFlex 900 SID recirculating chiller from Thermo Scientific. The ICP-OES has a concentric nebulizer and cyclonic spray chamber. The

instrument is provided with pure Ar(g) (N6.0) for both purging and the plasma. Table 3.4 gives the plasma parameters used in the study presented here.

Parameter	Value
Plasma Stabilization Time	10 min
Flush Pump Rate	50 rpm
Analysis Pump Rate	50 rpm
RF Power	1150 W
Nebulizer Gas Flow	0.6 L/min
Coolant Gas Flow	12 L/min
Auxiliary Gas Flow	1.0 L/min

Table 3.4: Plasma parameters.

The instrument can work in two modes: Radial view and axial view, as illustrated in Figure 3.6. Axial view is typically used for samples that require high sensitivity. However, axial view is limited in use by a relatively lower matrix tolerance and smaller dynamic range. On the contrary, radial view provides high matrix tolerance, but the sensitivity is reduced.



Figure 3.6: Illustration of the ICP-OES torch.

The instrument is equipped with an ASX-560 autosampler from Teledyne CETAC Technologies. To prevent cross contamination of samples, the autosampler is covered with a plastic enclosure, which is under suction. This also ensures the sample are protected from contamination from the surrounding environment.

#### 3.2.4 Reagents

All reagents were prepared using MilliQ water with a resistivity no higher than 18.2 m $\Omega$ . The water was purified using a Milli-Q<sup>®</sup> Advantage A10 Water Purification System. All samples used for the ICP-OES analysis was prepared using 2% nitric acid, prepared from a 70%, ACS reagent grade nitric acid.

All the standards used in the ICP-OES analysis (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup>) are of certified reference material grade, 10,000 mg/L in 5% HNO<sub>3</sub>. The internal standards (Y<sup>+</sup>, Sc<sup>2+</sup> and Cs<sup>+</sup>) are 1,000 mg/L in 5% HNO<sub>3</sub>. A commercial multi elemental standard is used as quality control (Multielement standard solution 3 for ICP). This contains 1,000 mg/L Na<sup>+</sup>, 200 mg/L K<sup>+</sup>, 400 mg/L Mg<sup>2+</sup> and 2,000 mg/L Ca<sup>2+</sup> in 5 HNO<sub>3</sub>. The daily performance is checked using a 2 ppm Zn solution, prepared from a 1,000 ppm Zn solution. All the reagents are listen in Table B.1. The plasma is fed with 5.0 Argon from AGA.

#### 3.2.5 Method development and testing

Two points are considered highly important when a method is developed:

- The methods shall provide accurate and reproducible results, and
- The methods shall be as straightforward as possible to follow, thus, limiting the risk of human error.

On the next pages, the developed method as well as an examination of the considerations undertaken the development of the analytical workflow with ICP-OES used in this project is presented.

The samples studied in this work are highly-saline. They are therefore known to contain high amounts of sodium (and chloride) relative to the other analytes. The expected average composition of a sample is presented in Table 3.5. The high sodium content is expected to affect our analysis. Firstly, possible spectral interference must be identified and the analytical wavelengths selected accordingly. Secondly, the calibration standards are matrix matched to limit the influence of physical-chemical interferences. Also, we must make sure our samples do not exceed the upper detection limit of the instrument. And lastly, the lower limit of detection for the analytes must be determined. The latter is especially relevant for  $Ba^{2+}$ .

Elemental ion	Concentration	Analytical technique	Analytical technique
	mg/L	Primary	Secondary
Na <sup>+</sup>	15,000 - 30,000	ICP-OES	IC
$Mg^{2+}$	200 - 1,200	ICP-OES	IC and ICP-MS
Ca <sup>2+</sup>	400 - 1,400	ICP-OES	IC
<b>K</b> +	100 - 400	ICP-OES	IC
$Sr^{2+}$	50 - 300	ICP-OES	ICP-MS
$Ba^{2+}$	<2	ICP-OES	ICP-MS
CI <sup>-</sup>	20,000 - 85,000	IC	-
$SO_4^{2-}$	100 - 400*	IC	-

**Table 3.5:** The average composition of produced water and the analytical technique(s) used.  $*SO_4^{2-}$  may reach 4,000 mg/L in a few samples.

In the initial method development model samples were used. These are prepared from inorganic salt dissolved in Milli-Q water to the desired concentrations.

#### Spectral interference: Choice of analytical wavelengths

Spectral interference is caused by the emission from two different ions at wavelengths close in energy and line broadening. As a consequence, the concentration of an ion may be overestimated if this is not mitigated. Two approaches to deal with spectral interference exist: Avoidance and correction. If possible, avoidance is favored. To avoid spectral interference, the analytical wavelengths must be chosen wisely. A list of wavelengths were initially chosen to be tested, from which the final analytical wavelengths were selected. The tested wavelengths are given in Table B.9.

More specifically, the potential spectral interference between ion pairs were tested systematically. First, two tests on the Na<sup>+</sup>-Mg<sup>2+</sup> interference were carried out. The first with constant Mg<sup>2+</sup> concentration and changing Na<sup>+</sup> concentrations. In the second test, both the concentration of Mg<sup>2+</sup> and Na<sup>+</sup> were varied. As a reference, pure samples containing only one element were analyzed. The specific concentrations are given in Table B.4. For Mg<sup>2+</sup>, three wavelengths were initially tested: 279.553 nm, 280.270 nm, and 202.582 nm. For Na<sup>+</sup>, two wavelengths were tested: 818.326 nm and 330.237 nm.

Secondly, a set of tests were run to check for spectral interference between the following ion pairs: Na<sup>+</sup>-Ca<sup>2+</sup> and Ca<sup>2+</sup>-Mg<sup>2+</sup>. Finally, a test for the full ion combination: Na<sup>+</sup>-K<sup>+</sup>-Mg<sup>2+</sup>-Ca<sup>2+</sup> was carried out. In all tests, the concentrations of the different ions were varied and the analyses were run at three wavelengths (and four for Mg<sup>2+</sup>). The details are given in Tables B.3 - B.10.

In the testing, no spectral - nor physical-chemical - interference between the elemental ions was observed. Consequently, the two wavelengths of highest intensity for all elemental ions were used in the forward analysis. Throughout the work, all elements were analyzed using two wavelengths as a minimum, as this functions as a quality check. The wavelengths used are given in Table 3.6. The concentrations reported in Chapter 5 (Study 2) in this thesis are the concentrations determined at the primary wavelength.

Elemental ion	Mode	Primary wavelength	Secondary wavelength
		nm	nm
Na <sup>+</sup>	Radial	589.592	818.326
K+	Radial	766.490	769.896
$Ca^{2+}$	Radial	422.673	315.887
$Mg^{2+}$	Radial	280.270	285.213
Y <sup>+</sup> (IS)	Radial	37	1.030
$Sr^{2+}$	Radial	407.771	421.552
$Sc^{2+}$ (IS)	Radial	36	3.075
Ba <sup>2+</sup>	Axial	455.403	493.409
$Sc^{2+}$ (IS)	Axial	36	1.384

**Table 3.6:** The selected mode and analytical wavelengths used for the mentioned ions in the ICP-OES analysis of produced water.  $Y^+$  and  $Sc^{2+}$  are internal standards (IS).

All analytes, but  $Ba^{2+}$ , are analysed in radial view as efficiently high intensities are achieved from it.  $Ba^{2+}$  [and  $Sc^{2+}$  (IS)] is analyzed in axial view for increased sensitivity.

#### Matrix match: Composition of calibration standards

The samples studied in this project have quite a complex matrix, and notably a high NaCl background. Based on the historical data, only minor changes in the produced water chemistry from sample to sample are expected, thus, allowing the use of the simple external standardization method. Fortunately, the approximate composition of the samples is known, as shown in Table 3.5. This is advantageous when deciding on the composition of the calibration standards.

The main challenge in our sample matrix is the high content of Na<sup>+</sup>. In the original samples, the Na<sup>+</sup> concentrations went up to, and for rare cases even exceeded, 40,000 ppm. Laboratory tests showed that the ionization suppression from Na<sup>+</sup> is too powerful at concentrations beyond 450 ppm. Hence, the Na<sup>+</sup> concentration in the analyzed samples may not exceed 450 ppm. To meet this, the samples are diluted 70-fold prior to analysis. This sets the starting point for the calibration curve. A four point calibration curve was used in this procedure. The final concentrations of the calibration standards are given in Table 3.7. The calibration curves are shown in Tables B.1, B.2 and B.3 and the calibration regressions are given in Table 3.7.

Elemental ion		Conce	ntration	in ppm		Calibration
Anions	C1	C2	C3	C4	Stock	regression
Na <sup>+</sup>	60	150	300	600	3,000	0.9582 - 0.9946
K+	0.2	0.5	1.0	2.0	10	0 9016 - 0.9992
Mg <sup>2+</sup>	1.4	3.5	7.0	14	70	0.9586 - 1
Ca <sup>2+</sup>	2.0	5.0	10	20	100	0.9575 - 1
Cations	C1	C2	C3	C4	Stock	
Na <sup>+</sup>	90	180	450	900	9,000	-
$Sr^{2+}$	0.5	1.0	2.5	5	50	0.9997 - 1
Ba <sup>2+</sup>	0.005	0.01	0.025	0.05	0.5	0.9952 - 0.9992

**Table 3.7:** The composition of the calibration standards used for the analysis of the bulk ions:  $Na^+$ ,  $K^+$ ,  $Mg^{2+}$  and  $Ca^{2+}$  - and of the trace ions:  $Sr^{2+}$  and  $Ba^{2+}$  - in produced water samples using ICP-OES.

Besides the ions mentioned in Table 3.5, the samples are expected to contain carbonate, bicarbonate, iodine, iron, phosphorous and various organic compounds. These are not included in the analysis using ICP-OES and IC and are not expected to impact the analytical results substantially.

#### 3.2.6 Internal standard

An internal standard (IS) is introduced to the sample to correct for variations in a) sample introduction efficiencies, b) sample matrix effects and, lastly, c) to adjust for instrumental drift. The internal standard is introduced to the sample through a Y-shaped joining piece before the sample reaches the instrument for analysis. Following the joining piece, the tube is shaped in a double loop to ensure fully mixing of the sample and the internal standard. This is illustrated in Figure 3.7. The IS is introduced to all liquids, including the calibration standards and the quality controls (QCs). The internal standard is present in all solutions at the exact same concentration.



Figure 3.7: Illustration of mixing and introduction of sample and internal standard. Artwork by the author.

#### Choice of internal standard

The IS element must be chemically stable and can not be naturally present in the blanks, calibration standards, quality controls nor in the samples. Otherwise, the concentration of the IS will be artificially affected by the fluctuations in the naturally occurring concentrations. Furthermore, the IS element must have similar ionization efficiency as the analyte(s) and be chemically stable when added to the sample. Lastly, the IS element must have emission lines similar to the analytes. Often, one of the rare earth elements are used as IS. These include yttrium and scandium.

For the analysis of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>, yttrium (Y<sup>2+</sup>) was used. [111] 50 mg/L is found to be a suitable level, considering the counts per second ( $\approx$  40,000 - 60,000 cps). A test was carried out to check if the Y<sup>2+</sup> signal was stable throughout an analysis. It was found that the intensity of Y<sup>2+</sup> decreases by up to 16% (from first to last sample) for an analysis including 40 samples; a week later, the decrease (from first to last sample) was 9% for an analysis including 88 samples. The software corrects the determined concentrations based on the reduction in IS intensity. In conclusion, Y<sup>2+</sup> performs well and shows good stability. For the analysis of Sr<sup>2+</sup> and Ba<sup>2+</sup>, scandium (Sc<sup>2+</sup>) is suggested. [111] 10 ppm and 20 ppm are proposed as appropriate levels of the IS. Thus, these levels were tested with sample-representable test solutions. At first, the instrument was calibrated using the calibration solutions given in Table 3.7. Next, a set of test solutions were run. These have similar, but not identical, compositions to the calibration solutions, the compositions are representable for the real samples, and they are prepared from a different stock solution. The compositions of the test solutions are given in Table B.11. The IS recoveries determined in the tests are given in Table 3.8.

IS test	IS recovery, %			Inten	sity, cps
	Radial	Axial	Blank samples	Radial	Axial
Sc 10 ppm	97-102	87-101	≈100	7,000 - 8,000	400,000 - 500,000
Sc 20 ppm	86-101	86-101	$\approx$ 100	17,000 - 19,000	> 1,000,000

Table 3.8: The recoveries of the IS in the test.

 $Sc^{2+}$  shows acceptable recoveries (preferably 95-105%) at both concentration levels. Though, 10 ppm  $Sc^{2+}$  shows recoveries slightly closer to 100% than 20 ppm  $Sc^{2+}$  does; consequently, 10 ppm  $Sc^{2+}$  is favored and is the IS that is recommended for this analysis.

#### 3.2.7 Vials and tubes

A vial test was undertaken to ensure the vials used for the analysis of the produced water samples did not release any contamination. Table B.12 lists the details of the vials that were exposed to the test. Overall, the vials differ very little. Vial no. 1 and 2 are 50 mL and conical. Vial no. 3 and 4 are both 15 mL; and vial no. 3 is conical, whereas vial no. 4 is round bottom. All the vials have screw caps and originate from different vendors. The vial test was conducted as follows:

- · One vial of each type was filled with MilliQ water, and
- One vial of each type was filled with 2% nitric acid.
- The vial were left for 48 hours and the liquids were analyzed on the ICP-OES.
- The analysis was repeated after 3 months.

All the analytical elements of interest (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup>) were included in the test. The acid is expected to be more aggressive, and, additionally, it is the most realistic scenario as the samples are diluted with 2% nitric acid. The test showed that Vial no. 2 released no contamination of any kind, not even after exposure for 3 months. Vial no. 1, no. 3 and no. 4 showed slight release of Ca<sup>2+</sup> (<0.1 ppm), which is more than 100-fold lower than the level of Ca<sup>2+</sup> found in the samples (even after the required dilution), therefore, this is not critical. Anyhow, when it is possible to choose a vial that realises no Ca<sup>2+</sup>, this is the one of choice, thus Vial no. 2 was used going forward.

As default phthalate-free PVC tubes (From Thermo Fischer Scientific) are used. Due to the slightly aggressive nature of the samples (acidic and organic components), wear of the tubing was observed after running approximately 50 samples or for two weeks with daily runs. Also, the tubes may get squeezed at the pump, leading to a non-circular cross-section, which can cause a non-uniform flow. Therefore, the tubing must be checked prior to an analysis. Squeezing of the tubing was never found to be the minimizing factor of the lifetime of the tubing. Whereas, chemical wear from the inside was. At the first sign of wear (observed as opaqueness), the tubing must be changed. Another organic-resistant tubing was tested (SPETEC, PU longlife, product no. 38-2030), but showed no improved lifetime.

# 3.2.8 Performance control and sequencing

At the start of every day a reference standard with  $2 \text{ mg/L Zn}^{2+}$  was run as a control for the daily performance. The minimum axial and radial intensity was 1,800 and 20000 counts per second (cps), respectively. If these criteria were not met, analyses were not to be run. Instead, a cleaning procedure had to be run: Tubing and the flow (tightness around the pump-wheel) must be checked and changed upon need. Also, all glassware - and especially relevant the purged optical path (POP)-window must be checked and cleaned if needed. The instructions set by the vendor was followed. Consistent results can be achieved only from proper maintenance.

Once passed, all analyses are started with a cleaning program, followed by the calibration curve including a blank. Secondly, the samples are run: Nine samples are run, followed by one QC sample and a wash containing 2% nitric acid. This is repeated until all samples have been analyzed. A blank (2% nitric acid) is randomly run at every 20-30 samples to check for carry over. Before shut down, a wash of 5% nitric acid, followed by 2% nitric acid is run to rinse the tubing.

#### 3.2.9 Quality control

Multielement standard solution 3 for ICP from Sigma Aldrich was used for quality control (QC) for cation analysis on ICP-OES; this contains 1,000 mg/L Na<sup>+</sup>, 2,000 mg/L Ca<sup>2+</sup>, 400 mg/L Mg<sup>2+</sup> and 200 mg/L K<sup>+</sup> and was chosen because it provides the best match with the composition of the samples. A 20- and 100-fold dilution of this was used as QC. For Sr<sup>2+</sup> and Ba<sup>2+</sup>, iCAP 6000 Multi Element test solution is used as QC. This contains, amongst other, 0.2 ppm Ba<sup>2+</sup> and is used undiluted.

#### 3.2.10 Sample preparation

The work presented in this thesis was aimed at analysing the elements already dissolved and present in the aqueous phase - and not at potential particulate matter. Therefore, simple dilution is sufficient for sample preparation (digestion is not needed). Before dilution, the samples are filtered using a 0.2  $\mu$ m nylon filter (Fisher Brand, catalog no. 15121499). This removes particulate matter and a potential minor organic phase, which helps to protect the hardware and minimizes the risk of blockage in the tubing. Particles may impact especially the ICP-OES and ICP-MS analysis.

For the ICP-OES and ICP-MS analyses, the filtered samples are slightly acidified, by dilution in 2 % HNO<sub>3</sub>. To match the linear range of calibration (Section 3.2.5), the samples are diluted 70-fold prior to the analysis on the ICP-OES.

# 3.3 Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)

ICP-MS is included as it has the capability of analyzing compounds present in low concentrations (<1 ppb). The included study is targeted on heavy metals, but do also cover  $Mg^{2+}$ ,  $Ba^{2+}$  and  $Sr^{2+}$ ; as this can function as a inter-instrumental test. The included study is the initial phase and was not completely finalized during this PhD study. Thus, the presented procedure is preliminary and shows great potential for improvement, which is discussed later in the thesis. The practical work of the ICP-MS analysis, including sample preparation, was carried out at the University of Copenhagen, Section for Environmental Chemistry and Physics. The method development was done in close collaboration with Sofie Nitsche Bergfors, who also did all the data treatment.

# 3.3.1 Samples

A subset of the previously described produced water samples from the four fields (section 3.1) was selected for this study. In total, 31 samples from Halfdan, 9 samples from Dan, 7 samples from Kraka and 8 from Valdemar were included. These were chosen to represent different wells, with preferably two samples from the same well, but sampled at different times.

# 3.3.2 Analytes and internal standards

The ICP-MS analysis covers 8 metals, see Table 3.9.  $Mg^{2+}$ ,  $Sr^{2+}$  and  $Ba^{2+}$  are also analyzed with ICP-OES, thus an inter-instrumental test can be carried out; and enabled a validation of the results achieved with the ICP-MS. For optimal analysis, four different internal standards are used. These were chosen to fit the m/z (rather than the ionization potential) and are also listed in Table 3.9, see also Section 3.3.5.

Analyte	Mass	Mode(s)	Internal standard
Mg	24	No gas + He	Ge (72)
Mn	55	No gas + He	Ge (72)
Zn	66	He	Ge (72)
As	75	He	Ge (72)
Sr	88	No gas + He	Y (89)
Ва	137	No gas + He	Ce (140)
Hg	202	No gas + He	lr (193)
Pb	208	No gas + He	lr (193)

**Table 3.9:** Analytes included in the ICP-MS analysis; and the mass, mode(s) and internal standard used in the analysis.

# 3.3.3 The instrument

Element concentrations in the samples were quantified using a 7900 ICP-MS from Agilent. The instrument was run in high-matrix (HMI) mode, with a SeaSpray U-Series nebulizer (0.4-1.0 mL/min, Glass Expansion), connected to a cooled spray chamber (2 °C, Scotts double pass). The sample mist was introduced to an argon plasma operating at 1600 W with 15 I Ar per minute. The skimmer and sampler cone consisted of nickel and the lenses

were the Agilent X-lens configuration.

All samples were analyzed in both "no gas mode" for best sensitivity and "He mode" for removing interferences. The He flow in the cell was 5.0 mL/min. Further plasma settings are given in Table 3.10.

Parameter	Value
RF Matching	2.0 V
Sampling depth	10 mm
Carrier gas flow	0.68 L/min
Dilution gas flow	0.27 L/min
Nebulizer pump speed	10 rps

Table 3.10: Plasma parameters for the ICP-MS analysis.

All samples were analyzed in four replicates, which were averaged. Every measurement includes 30 sweeps per replicate. The resulting total acquisition time per sample was 3 minutes and 57 seconds. Between every sample, the injection syringe was cleaned in acid solution to avoid contamination and carry-over. Signals were reported in ICP-MS MassHunter 4.3 G7201C (Version C.01.03/ Build 505.23, Patch 4). The used m/z-values and integration times used for the quantification of the analytes and internal standards (IS) are given in Table 3.11.

Analyte	m/z	Integration time, s
Mg	24	0.5
Mn	55	0.5
Ge (IS)	72	0.5
Sr	88	0.5
Y (IS)	89	0.5
Ba	137	0.5
Ce (IS)	140	0.5
Ir (IS)	193	0.5
Hg	202	1.0
Pb	208	0.5

Table 3.11: Quantification parameters for the ICP-MS analysis. (IS) denotes the internal standards.

#### 3.3.4 Calibration

The calibration standards are prepared in either pure water or in a solution of synthetic seawater, prepared after "ASTM D1141-98 Standard Practice for the Preparation of Substitute Ocean Water". The composition is given in Table 3.12.

Salt	Amount, g/L
NaCl	24.53
$MgCl_2$	5.2
$Na_2SO_4$	4.09
$CaCl_2$	1.16
KCI	0.695
NaHCO <sub>3</sub>	0.201

Table 3.12: ASTM D1141-98 recipe for synthetic seawater.

The same calibration standards are used for both "No gas" and "He" modes. The composition of these is given in Table 3.13.

	Concentration, $\mu$ g/L							
Element	C1	C2	C3	C4	C5	C6		
$Mg^{2+}$	1000	100	10	1	0.1	0.01		
$Mn^{2+}$	1000	100	10	1	0.1	0.01		
$Zn^{2+}$	1000	100	10	1	0.1	0.01		
$As^{2+}$	1000	100	10	1	0.1	0.01		
$Sr^{2+}$	1000	100	10	1	0.1	0.01		
$Ba^{2+}$	1000	100	10	1	0.1	0.01		
$Hg^{2+}$	1000	100	10	1	0.1	0.01		
$Pb^{2+}$	1000	100	10	1	0.1	0.01		

 Table 3.13: Composition of calibration solutions for analysis using ICP-MS.

The internal standard is introduced similarly as in the ICP-OES analysis. This is illustrated in Figure 3.7. A quality control containing 10  $\mu$ g/L of all the analytes is run for every five samples.

# 3.3.5 Mass Spectrometry

Mass Spectrometry (MS) is an analytical technique, where one or molecules in a sample are measured and identified based on their mass-to-charge ratio (m/z). These measurements can often be used to calculate the exact molecular weight of the sample components and, often, it can also be used to determine structure and chemical properties of the sample molecules. Later, in Section 3.5, MS is used to identify organic components, which is also one of the most typical applications of MS. In this work, MS is used to identify elemental ions. Going from ICP-OES to ICP-MS, a sensitivity increase of approximately a factor of 100 is achieved. To avoid sample upconcentrations, this increased sensitivity is needed for the analysis af the heavy metals in the produced water samples, as they are present in trace amounts.

A MS consists of at least three elements: An ionization source, a mass analyzer and an ion detection system. In this work, the ICP is the ionization source and a single quadrupole is employed as the mass analyser. This contains four parallel cylindrical metal rods placed inside a vacuum chamber and positioned evenly from the center axis, as illustrated in Figure 3.8. The rods are collected in two pairs of opposite rods. To each of the rod pairs, a radio frequency voltage is applied; this has a direct current offset voltage between the

pairs. Ions travel down the quadrupole between the rods and will as a consequence of the electrical field, oscillate in the X and Y directions. Depending on the field and the m/z ratio of the ions, they will either travel trough to the detector, or become unstable, causing them to collide with the poles, and, consequently, not be detected.



#### Figure 3.8: Illustration of a quadrupole mass analyser. From Spectroscopy Europe. [74]

#### 3.3.6 Sample preparation

The produced water samples are prepared similarly as for the analysis on the ICP-OES (see Section 3.2.10). The samples are filtered using a 0.2  $\mu$ m nylon filter. Any following treatment of the samples is discussed in Chapter 7.

# 3.4 Ion Chromatography (IC)

Ion chromatography (IC) is a chromatographic method that separates charged molecules or elements (ions) based on their affinity to the ion exchanger. IC has higher matrix tolerance than most other separation techniques because only one interaction is involved in the separation. Another advantage is that the elution pattern is highly predictable and the output is, therefore, often easily analysed. A disadvantage of IC is that the effective analysis time is much longer (10-fold) than for example for ICP-OES.

Routine analysis of the anions,  $CI^-$  and  $SO_4^{2-}$ , are carried out using IC. Also, interinstrumental control analysis of the cations Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> using IC is carried out.

# 3.4.1 Instrument and columns

The instrument used is a Dionex Integrion HPIC (High Pressie Ion Chromatography). It has an IonPac<sup>TM</sup> CG16-4 $\mu$ m, RFIC<sup>TM</sup>, 4 x 50 mm guard column. The guard column serves to remove possible impurities and suspended solids in the sample, to avoid the risk of them reaching the analytical column. For the anion analysis, a Dionex<sup>TM</sup> lonPac<sup>TM</sup> AS22, RFIC<sup>TM</sup>, 4 x 250 mm analytical column is used (product number 064139). For cation analysis a Dionex<sup>TM</sup> IonPac<sup>TM</sup> CS16-4 $\mu$ m, 4 x 250 mm analytical column is used (product number 088584). In both columns, the charged molecules/ions are separated based on their affinity towards the exchange sites in the columns. After the column, the eluent and sample ions flow through a suppressor. The suppressor selectively enhances detection of the sample ions while it simultaneously decreases the background signal and noise. For the anion analysis, the suppressor is a Dionex<sup>TM</sup> AERS<sup>TM</sup> 500 Carbonate Eletrolytically Regenerated Suppressor, 4 mm (product number 085029); and for the cation analysis a Dionex<sup>TM</sup> ERS<sup>TM</sup> 500e Cation Electrolytically Regenerated Suppressor is used (product number 302663). The gradient mixer is a Dionex<sup>TM</sup> GM-4, 2mm (product number 049136). The samples are detected with a conductivity detector (CD). and Thermo Scientific<sup>TM</sup> Dionex<sup>TM</sup> Chromeleon<sup>TM</sup> 7 Chromatography Data System is used for the data analysis.

The instrument is equipped with a Dionex<sup>TM</sup> AS-DV autosampler (catalog number 068907), which takes 5 mL vials. 5 mL PolyVials<sup>TM</sup> from Thermo Scientific are used for all samples, standards and QC solutions (P/N 038009); these are sealed with a filter cap.

# 3.4.2 Reagents

All reagents were prepared using Milli-Q water with a resistivity no higher than 18.2 m $\Omega$ . The water was purified using a Milli-Q<sup>®</sup> Advantage A10 Water Purification System. 30 mM methanosulforic acid is used for the cation analysis and sodium carbonate (4.5 mM)/bicarbonate (1.4mM) (from Dionex<sup>TM</sup> AS22 Eluent concentrate) is used for the anion analysis. The IC single element standards (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>) are of certified reference material grade, 10,000 mg/L in water. For the anion analysis, Dionex<sup>TM</sup> Combined Five Anion Standard was used as quality control. For the cation analysis, no quality control was run, as the analysis already functions as a control for the ICP-OES analysis.

A list of all the chemicals, with specifications, is given in Appendix B, Table B.1.

# 3.4.3 Calibration and method

The IC anion analysis is targeted to the quantification of  $CI^-$  and  $SO_4^{2-}$ . The samples were expected to contain other anions as well, for example  $Br^-$  and  $HCO_3^-$ , in concentrations low enough to not impact the analysis of  $CI^-$  and  $SO_4^{2-}$ . A four-point calibration is used for the anion analysis; the concentrations are given in Table 3.14.

The IC cation analysis (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>) covers all ions of relevance for the IC analysis in the sample (considering the concentration of the ions, which exclude  $Sr^{2+}$  and  $Ba^{2+}$ ). A three-point calibration is used for the cation analysis; the concentrations are given in Table 3.14. The calibration curves are shown in Appendix B, Figures B.5, B.6 and B.7 and the calibration regressions are given in Table 3.14. The calibration regressions are given in Table 3.14.

						Calibration		
	Element	Concentration, mg/L				regression		
Anions		Std 1	Std 2	Std 3	Std 4			
	CI <sup>-</sup>	40	60	80	100	0.9931 - 0.9981		
	$SO_4^{2-}$	1	2	5	10	0.9976 - 1		
Cations		Std 1	Std 2	Std 3				
	Na <sup>+</sup>	88.2	114.2	137.2		0.9526 - 0.9999		
	$K^+$	2.3	4.6	6.9		0.9996 - 1		
	$Ca^{2+}$	1.1	5.7	11.5		0.9996 - 1		
	$Mg^{2+}$	11.1	17.3	23.0		0.9867 - 1		

Table 3.14: Composition of calibration standards for the analysis of anions and cations using IC.

The chromatograms for a set of calibration standards and three different samples are given in Appendix B, Figures B.8, B.9 and B.10 for Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> and Appendix B, Figures B.11, B.12 and B.13 for Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>, respectively.

The specific experimental parameters for IC analyses are given in 3.15.

Parameter	Anion analysis	Cation analysis
Gradient type	Multi-step gradient	Isocratic
Flow	1.2 mL/min	0.64 mL/min
Pressure lower limit	200 psi	200 psi
Pressure upper limit	2,000 psi	4,000 psi
Pump delivery speed	4.0 mL/min	4.0 mL/min
Flush factor	10	10
Sample deliver	2.5 mL	2.5 mL
Sample delay volume	125 $\mu$ L	125 $\mu$ L
Column temperature	30.0°C	430.0°C
Temperature compensation	1.7%	1.7%
Data collection rate	5.0 Hz	5.0 Hz
Total time	15 min	28 min

Table 3.15: Parameters for the analysis on the Ion Chromatograph (IC).

# 3.4.4 Quality control and sequencing

Dionex<sup>*TM*</sup> Combined Five Anion Standard from ThermoFischer was used as quality control (QC) for the anion analysis. This contain 30 mg/L Cl<sup>-</sup> and 150 mg/L SO<sub>4</sub><sup>2-</sup>. Two QC solutions were prepared from a 100- and 1000-dilution of this. For the cation analysis, no quality control was run, as the analysis already functions as an control for the ICP-OES analysis.

Before the analysis is initiated, the instrument is purged and left to flush with eluent for a minimum of 20 min, or until the current detected has stabilized and has remained stable for a minimum of 4 min. All analytical runs are initiated with a blank sample, followed by the calibration standard solutions. Next, a set of QCs are run, before the samples are run. For every ten samples, a set of QCs is run, followed by a blank sample. It is noted, that for the cation analysis, the QCs are substituted with the full set of calibration standards. At the end of an analytical run, a set of QCs (for the cation analysis, this is the full set of calibration standards) and a blank are run. The QCs are used to check for instrumental drift, and the blanks are used to check for carry-over effects. No significant drift, nor carry-over is observed in any of the analyses.

# 3.4.5 Sample preparation

Filtration and simple dilution is carried out prior to the IC analysis. The filtered samples are diluted 1000-fold using MilliQ water for the analysis of the anions (CI<sup>-</sup> and SO<sup>2-</sup>) and 100-fold for the analysis of the cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>).

# 3.5 Gas Chromatography x Gas Chromatography - High Resolution Mass Spectrometry (GCxGC - HRMS)

Gas chromatography (GC) is an analytical technique used to separate chemical compounds in a sample mixture. Usually, these compounds are gaseous or organic molecules. In this work, we use GC to study organic molecules in produced water samples. For the analysis to be successful, the sample components (organic molecules) must be relatively volatile. Often this is achieved for molecules with a molecular weight below 1250 mD. As the name implies, in GC, a carrier gas is used to drive the sample through the column, where the separation takes place. Ideally, the carrier gas does not react with the samples (or damage the instrument components). The samples analyzed in the presented work contain a very complex organic mixture, thus, to achieve a sufficiently high peak capacity, a second dimension GC is introduced. For the detection of the sample components, the GCxGC is coupled to a quadrupole time-of-flight (QTOF) high-resolution mass spectrometer (HRMS). Prior to the analysis, the samples are extracted from the water phase to an organic solvent using liquid-liquid extraction (LLE). For all samples, three replicates were prepared and analysed.

#### 3.5.1 Instrument and data processing

The analysis was carried out using an Agilent 7890B GC coupled to a 7200B QTOF highresolution mass spectrometer (Agilent Technologies, Palo Alto, CA, USA). The system was equipped with a Zoex ZX-2 thermal modulator (Zoex Corporation, Houston, TX, USA). For the separation, a combination of an Agilent DB-5MS UI (1D, 30 m, 0.25 mm i.d., 0.25  $\mu$ m df) column [1D] and a Restek Rxi-17Sil MS (2D, 2 m, 0.18 mm i.d., 0.18  $\mu$ m df) column [2D] was used. These were connected using a SilTite  $\mu$ -union.

An oven is used to heat the column and support the vaporisation of less-volatile sample components. The temperature program is given in Table 3.16. The program was run in constant flow mode (1 mL/min).

Туре	Temperature	Time/ramp
Hold	50°C	1 min
Ramp	320°C	3°C/min

 Table 3.16:
 Temperature program for the GCxGC analysis.

The modulation period was set to 3 s with a 400 ms hot-jet duration. The transfer line to the mass spectrometer was held at 280°C. Electron ionization mode (70 eV) was used to acquire the spectre on the MS. It has a mass range of 45 – 500 and an acquisition speed of approximately 50 Hz. The dynamic range was increased by operating the instrument in its 2 GHz sampling rate mode. Automatic mass calibration was performed for every fifth sample (approximately every 7.5 hours).

Peak detection and library search were performed using GC Image v2.8.3 (Zoex, Houston, TX). All mass spectra were matched against the NIST Mass Spectral Library (National Institute of Health, 2017 edition). The threshold for a compounds match was set at a minimum match factor of 700. All feature tables (match compounds) were exported as comma-separated texts for additional data processing externally. for this, a data processing pipeline was created in-house in Python (Python Software Foundation. Python

Language Reference, version 3.7.4. Available at http://www.python.org). The data processing pipeline was used to reduce the enormous data set achieved by the GCxGC analysis. A first step was to increase the confidence level for the identification of components. For this, the following scoring rules based on scoring match with the NIST database were implemented.

- A match factor above 800 gives a score of 10 points.
- A match factor between 700 and 800 gives a score of 5 points.
- A retention index match within 50 units gives a score of 5 points.
- The detection of the molecular ion (within 20 ppm mass accuracy) gives a score of 5 points.

Furthermore, only features that were present in all three replicates were included in the final feature table and all compound duplicates were removed.

# 3.5.2 2D gas chromatography

Conventional 1D chromatography does not offer the required peak capacity it takes to resolve the compounds in the samples presented in this work as these are highly complex mixtures. One option to circumvent this limitation is to use pre-fractionation of the samples (i.e. solid-phase extraction and its derivatives) - or by implementing multi-dimensional chromatography. If available, the latter is advantageous as it implies less cumbersome sample pre-treatment. Under optimal conditions, 2D chromatography can reach an experimental peak capacities of up to 10,000. [21, 33, 117] A secondary advantage is that column bleed, i.e. cyclic siloxanes, is not retained by a polar 2D column. Consequently, high background levels of siloxanes (caused by the high temperatures) are removed. In GC×GC, the two columns are chosen to posses orthogonal separation chemistry. Consequently, co-eluting peaks from the primary column are separated on the secondary. [22, 50] This principle is illustrated in Figure 3.9.



**Figure 3.9:** Principle of comprehensive two-dimensional gas chromatography. Compounds are separated based on volatility in the first dimension and based on polarity in the second dimension. Pictures from Thermo Fischer, presented with modification. [23]

The effluent from the 1D is injected as plugs into the 2D by a modulator. It is crucial that the secondary column is shorter than the primary column. This ensured that all species have eluted from 1D before they are injection into the 2D column. Three modulations per peak were achieved using a modulation period of 3 s.

The water samples are expected to contain mainly heteroatom-containing analogs of hydrocarbons, which have partitioned to the water phase due to their polarity. The organic compounds in the produced water are expected to vary by 1) having the same core with different degrees of alkylation, i.e. volatility range, and 2) having the same core and alkylation but varying degrees of oxygenation (or presence of other heteroatoms), i.e. polarity range. It is expected that the variance in the volatility exceeds the variance in the polarity. Therefore, the we choose to use a non-polar column in the first dimension, which has the highest separation power, and a, shorter, polar column in the second dimension. A 50%phenyl-type column was used for the second dimension. Conventional polar columns are based on polyethyleneglycol (PEG) chemistry, but these are incompatible with silylation derivatization reagents and, thus, not a preferred choice for this study.

Retention time shifts are commonly observed both in inter-sample and inter-batch runs due to experimental complexity and long run times. These shifts over time were monitored using deuterated PAH standards.

# 3.5.3 Samples and sample pre-treatment

A subset of the previously described produced water samples from the Halfdan field (section 3.1) was selected for this study. In total, nine samples, were included. These were chosen to represent different wells, with preferably two samples from the same well, but sampled at different times. Immediately after arrival to the laboratory, a subsample was 100 mL was transferred to 100 mL glass bottle, and treated with dilute hydrochloric acid for preservation (18%, 0.1 mL per 100 mL sample).

#### Liquid-liquid extraction

To allow the analysis on the GCxGC, the organic compounds were extracted using liquidliquid extraction (LLE). First, the samples were filtered through a 0.45 µm PTFE-filter to remove undissolved components. Subsequently, 50 mL of the samples was extracted with 50 mL dichloromethane (DCM). The organic phase was washed with 50 mL brine (saturated NaCl) and removed in vacuo. The residue was reconstituted in 1.5 mL nhexane and dried over MgSO<sub>4</sub>. 1000 µL of the reconstructed sample was transferred to a 2 mL vial. Here, it was combined with deuterated internal standards, combined with 50 µL BSTFA+TMCS [N,O-Bis(trimethylsilyl)trifluoroacetamide+trimethylchlorosilane] for derivatisation and incubated at 70°C for 30 min. Following this step, the derivatised sample was allowed to return to room temperature and diluted to an appropriate concentration with n-hexane. Subsequent, the samples was analyzed on the GC×GC-MS. All samples (including procedural blanks, see below) were extracted in three experimental replicates using separate glassware.

# 3.5.4 Extraction recovery and reproducibility test

A synthetic produced water containing six representative model compounds in simulated formation water was prepared to determine the variability in the sample preparation protocol and the instrumental analysis. The synthetic water contains benzoic acid, phenol,

2-naphthoic acid, cyclohexanecarboxylic acid, and octanoic acid; each at 5 ppm, thus, is has a total organic concentration of 30 ppm. The synthetic water was extracted six times in two batches. Three procedural blanks were prepared to establish background levels and experimental sources of contamination.

# 3.5.5 Chemicals and reagents

High purity water was obtained from a Milli-Q Advantage A10 unit. An 1D retention index calibration was performed using a linear C7 to C30 saturated alkanes mixture. The used chemicals are listed in Appendix B, Table B.16. All chemicals and reagents were used as received from the supplier.

# 3.5.6 High Resolution Mass Spectrometry (HRMS)

A quadrupole time-of-flight (QTOF) mass analyser is applied for the study of the organic components in the produced water. This advantageously combines the benefits of two different mass analysers; from the quadrupole a high compounds fragmentation is utilised. This is combined with the high mass resolution capability of the time-of-flight, gaining an extremely selective and sensitive mass analyser.

In the TOF, compounds are separated in space based on their travel-time through a fixed distance in the flight tube: The sample ions are accelerated by an electric field of a known strength. From the acceleration, all ions of same charge have the same kinetic energy. The velocity of an ion then depends on the mass-to-charge (m/z) ratio of that specific ion. Thus, the travel-time will be different for ions of different m/z-ratios. At the detector, the travel-time at a known distance is detected. It always holds that heavier particles travel slower than lighter particles.

# 4 Study 1: Characterisation of and changes within formation water types

# 4.1 Short introduction

In this study, we present and discuss an analysis of the ionic composition of produced water from four oil producing chalk fields in the Danish North Sea. The produced water chemistry (PWC) is interpreted to shed light on the temporal and regional variations in the water composition. End-members (or water types) are classified and may be input for eg. reservoir simulations; design of core-flooding experiments, scale and corrosion experiments and to predict the risk of scale formation at the fields. The full study is presented in Paper 1, Appendix A.1. [96]

The presented study is based on produced water chemistry (PWC) data from four fields in the Danish North Sea: Dan, Halfdan, Kraka and Valdemar. The data contains the sample location (well name), sampling date and the concentrations of eight ions: Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. In total 8749 data series are included; covering 161 wells, with the majority of the data from the Dan and Halfdan fields. The data has been collected from beginning of production for the different fields and up to and including 2015. It shall be noted that water injection is employed at the Dan and Halfdan fields.

Principal component analysis, PCA, is applied to analyse the data. It is a multivariate data analysis method that can be used to reveal hidden data structures; trends and outliers. [17, 52] The input data is converted into linearly uncorrelated variables by the use of orthogonal transformation. The output uncorrelated variables are called the principal components (PC). The first principal component (PC-1) lies along the direction of the maximum longitudinal variance in the data set and the second PC (PC-2) lies along the direction of the second largest variance orthogonal to PC-1. [53] The PCA is performed with The Unscrambler X 10.5.1 software package. [20, 52] Prior to the analysis, the data is center log ratio (clr) transformed. [55, 80]

ScaleCERE is a program based on the Extended UNIQUAC thermodynamic model, which is designed for electrolyte solutions. The program is used to predict the risk of scale formation for the produced water; as described in details by K. Thomsen. [59, 113]

# 4.2 Main findings

# **Temporal changes**

Figure 4.1 shows the temporal changes in the PWC for one representative well in each of the three fields Dan, Halfdan and Valdemar. The Kraka field is not included here as the available data is too sparse for a solid discussion. Figure 4.1 shows a stabilisation in the PWC at the Dan and Halfdan field at the same time as injection water breakthrough. At this time, a shift in the  $Ca^{2+}/Mg^{2+}$  ratio is observed; this may be caused either by 1) mixing of formation water (rich in  $Ca^{2+}$ ) and injection water, or 2) cation exchange on the chalk surfaces inside the reservoir or 3) a combination of the two. The Valdemar field is significantly different than the Dan and Halfdan fields; the salinity (NaCl) of the Valdemar

field is much lower. Furthermore, the Valdemar field shows a long clean-up time; shown as a slow stabilisation in the concentration of  $K^+$ , which is found in the mud system used for the completion of wells. [88] This is most likely caused by the low permeability found at the Valdemar fields, which is the least permeable of the four fields included.



**Figure 4.1:** Temporal changes in the water composition of produced water from the following fields: Well A: Halfdan, Well B: Dan, and Well C: Valdemar. For the wells, plots A, C and E show the changes in the concentrations of Na<sup>+</sup> and Cl<sup>-</sup> and plots B, D and F show the evaluation of K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>. The blue curve gives the water cut (vol % water) of the produced liquid (right axis). The water cut for the Valdemar field has not been provided. Arrows mark occurring event.

#### Intra-field variations

The intra-field variations of the PWC are analyzed for the Halfdan and Dan fields.  $Ba^{2+}$  was removed from the analysis as it caused disordered model results. [2, 43, 81]

The wells from the Halfdan field are divided into six sections: North East, North Central, North West, South East, South West and Spine, as shown in Figure 4.5. The PCA results are shown in Figure 4.2. It is found that the most saline water is produced from Halfdan Southwest, Halfdan Northeast has the weakest  $SO_4^{2-}$  component, suggesting it is the region that is the least affected by (sea)water injection. Halfdan North Central and Northwest display very similar PWC, signified with showing the largest spread in the PWC. The strongest Na<sup>+</sup>-Cl<sup>-</sup> component is observed at Halfdan South West, which suggests this is the most saline water.



Figure 4.2: PCA of PWC from the Halfdan field divided into five geographically defined groups. A) PCA score plot and B) PCA loading plot of PC-1 vs. PC-2.



**Figure 4.3:** PCA of PWC from the Dan field divided into two geographically defined groups. A) PCA score plot and B) PCA loading plot of PC-1 vs. PC-2.

At the Dan field, the wells are divided into two groups: Wells from the Northwestern flank facing the Halfdan field and the remaining wells that are situated on Central Dome. The PCA results are shown in Figure 4.3. The PWC from the Central Dome shows a large spread, whereas, the water from the Northwestern flank has a more uniform chemistry. The water from the latter, shows less extreme salinities and  $SO_4^{2-}$  levels; thus, it is less influenced by production chemicals.

#### Inter-field variations and classification of water types

A PCA plot of the inter-field variations is displayed in Figure 4.4. Samples from Dan and Halfdan are found to plot together; showing they have the same chemistry, which suggests the water produced at the two fields either 1) have the same origin, or 2) migrates through the fields, suggesting that the two fields are connected. The water produced at Halfdan and Dan moves towards a seawater signature caused by the water flooding. The Valdemar field is signified by a high Ba<sup>2+</sup> level, low SO<sub>4</sub><sup>2-</sup> and high K<sup>+</sup>; caused by the effect of completion fluids. The water produced at the Kraka field is highly saline and shows a strong Sr<sup>2+</sup> component.



**Figure 4.4:** Regional changes in the water composition across all four fields. A) PCA score plot and B) PCA loading plot of the PC-1 and PC-2 axis. The boxes represent the five localized end-members (EM1-EM5). These are defined in Table 4.1.

From the PCA plot shown in Figure 4.4, five end-members ("water types") are classified. The compositions of these are presented in Table 4.1 together with the typical occurrence of the water type.

#### Fluid dynamics in the Halfdan-Dan area

As briefly touched upon earlier, similarities in the PWC from the Dan and Halfdan fields are observed (Figure 4.4). This suggests that the waters either have the same origin or that there is a migration of water through the fields. Albrechtsen *et al.* proposed that hydrodynamic forces drive the water towards southwest in the Halfdan field due to a tilting of the area. [101] Figure 4.5 displays this model. According to the proposed model, the water is expelled from the Sif and Igor area located northeast of the Halfdan field. When the relevant rates and distances are taken into consideration, the water from the Halfdan

End-member	Na <sup>+</sup>	$K^+$	$Mg^{2+}$	$Ca^{2+}$	$Sr^{2+}$	$Ba^{2+}$	CI-	$SO_4^{2-}$
Typical occurrence	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
1	15931	154	210	891	91	12	27003	42
Halfdan N.								
2	10994	379	1241	480	5.0	1.0	20049	2352
"Seawater"								
3	26648	210	408	2611	328	1.0	47023	560
Dan (and Halfdan S.)								
4	10211	122	100	371	65	45	16881	36
Valdemar								
5	41546	210	514	2671	363	1.0	70493	482
Kraka								
Seawater [15]	10780	400	1280	410	20	0.0	19350	2710

Table 4.1: The composition of the localized end-members (EM) given in mg/L.

field have passed through the Dan field by now. [56] This model fits the presented data, where a general increase in salinity from the eastern part of the Halfdan field across the Dan Northwest field and to central parts of Dan is observed.



**Figure 4.5:** Flow model. Contour map of the top chalk (scale in feet) showing the Skjold-Halfdan-Dan-Igor area. The geographical division of the Halfdan (NE, NC, NW, SE, SW) and Dan (NW and CD) fields is shown with colored boxes. Relative fluid transport directions of oil, gas and water are from Albrechtsen *et al.* [101] The outline of the production well patterns are from the Danish Energy Agency. [15] The median concentrations of  $CI^-$  and  $SO_4^{2-}$  for each area are in mg/L.

The salinity is first order controlled by the presence of salt domes and pillows.

#### **Risk of scale formation**

In many oil fields in the Danish North Sea, including the Halfdan field, scale has proven to be a significant risk in some wells. [107] These scale includes  $CaCO_3$  and the less soluble scales  $SrSO_4$  and  $BaSO_4$ . [39, 63, 97, 98, 109] The most used indicator the the risk of scale formation is the PWC. Especially the concentration of  $Sr^{2+}$  and  $Ba^{2+}$ , and slight variations therein, are important. Water flooded reservoirs may be especially relevant as the injection water often introduced large concentrations of  $SO_4^{2-}$ . The classified endmembers (EMs) have been subject to scale prediction calculations using the ScaleCERE program. From this, it is found that both  $CaCO_3$  and  $BaSO_4$  is a risk for all EMs. EM4 (the Valdemar field) is found to be the most sensitive.  $SrSO_4$  is a risk at EM3 (Halfdan South) and EM5 (Kraka) and only at reservoir conditions. The increased sensitivity upon seawater injection is confirmed for  $SrSO_4$  and  $BaSO_4$ .

#### Implications for production strategies

Currently, the mechanism behind enhanced oil recovery is still discussed and several mechanisms are proposed. [8, 18, 84, 102, 109, 111] However, Ca<sup>2+</sup>, Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> are believed to the most important ions affecting the recovery. Puntervold, Strand, and Austad have proposed an optimal concentration ratio of the determining ions to obtain the best possible recovery: Mg<sup>2+</sup>  $\approx 2 \cdot SO_4^{2-} \approx 4 \cdot Ca^{2+}$ . [109] This relative composition is not found in any of the identified end-members, which suggests it may be possible to optimize the injection water further to improve the recovery.

# 5 Study 2, part 1: Produced water from the North Sea – A case study and analytical guidelines

# 5.1 Short introduction

The work presented in Study 1: "Classification of and changes within formation water types in Danish North Sea Chalk: A study of the Halfdan, Dan, Kraka and Valdemar oil reservoirs", is based on historical data from chemical analysis of produced water samples - the data covers the concentrations of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. During this study, questions started to arise regarding the reliability and accuracy of the presented data. Ion chromatography (IC) was used to measure the concentrations of all the ions. The lower limit of detection (LOD) with this workflow was 1 mg/L. This has two major consequences: In many of the samples, the concentration of Ba<sup>2+</sup> is below the LOD of the IC. The Ba<sup>2+</sup> and Sr<sup>2+</sup> concentrations, and small variations therein, are important input for scale monitoring and mitigation strategies. Secondly, small changes in the concentration of the remaining ions may not be detected. This applies, for example, to Ca<sup>2+</sup> and Mg<sup>2+</sup>, whose concentrations may change slightly due to cation exchange with the reservoir rock. [96] Exchange processes at the surface is a typical mechanism proposed for enhanced oil recovery. [54, 64, 69, 84, 86, 90, 102, 109] Thus, a validation of the historical data - and the development of a new analytical workflow with a lower LOD is requested for future analysis of produced water.

The study presented in this chapter describes an analytical workflow for the analysis of produced water combining IC with Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) for the analysis of the cations: Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup>. IC is used to analyse CI<sup>-</sup> and SO $_4^{2-}$ , as only cations can be detected using the ICP-OES. The LOD for ICP-OES is parts per billion (µg/L), thus a factor of 1000 smaller than for common IC analysis. Furthermore, the ICP-OES can analyze up to 30 elements in one sample and is well suited for high-salinity samples (up to 30% TDS), like the samples presented in this study. Finally, the time for the analysis of one sample (excluding instrument start-up) is about a factor of ten shorter for ICP-OES than IC. The main drawback of the ICP-OES is that it analyzes only cations. Opposite, an IC can analyze both cations and anions. However, independently of the analytical method chosen, the analysis of cations and anions must be done separately. In produced water, the concentrations of the anions (Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) are present at mg/L level, whereas Ba<sup>2+</sup> is present in  $\mu$ g/L levels only. Thus, the combination of ICP-OES for cations and IC for anions is found extremely powerful for the analysis of the produced water (and alike) samples. The methods are described in details in Section 3.2 and 3.4.

The new analytical workflow is presented along with an evaluation of the new and the old analytical techniques, including an inter-instrument and inter-laboratory test as results must be reproducible. The Halfdan field is used as case study. Figure 5.1 show a visual-isation of the presented study.



**Figure 5.1:** Visualisation of the presented study. ONS = Operator New Samples, OND = Operator New Data, DNS = DHRTC New Samples.

Parity plots are used to compare the results. In all plots, the one-to-one correlation is shown together with the  $\pm 25\%$  deviations from the one-to-one correlation. In the comparison and discussion of the results, all points within the  $\pm 25\%$  deviation are included unless otherwise is stated. Thermodynamic modelling, using ScaleCERE, is included to predict the scale potential based on the Ba<sup>2+</sup> concentrations determined using the new analytical workflow including ICP-OES. [59, 113]

As part of the work going into this study, a protocol describing the analytical workflow in details was made. This is attached in appendix A.4. The full study and experimental workflow is described in details in the attached manuscript A.2.

# 5.2 Main findings

# Experimental results compared to reported results

Figure 5.2 shows a comparison of data received from the operator (Operator New Data = OND) and the experimental results (DHRTC New Samples = DNS) of similar samples; 32 samples are included. The linear trendlines equations and their regression coefficients are given in Table 5.1 together with the number of points excluded from the trend. Overall, good agreement between OND and DNS is observed. From the trendline slopes, it is found that the concentrations of K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> are highest in DNS. Opposite, the concentrations of Na<sup>+</sup> and Sr<sup>2+</sup> are highest in OND. That no consistent trend is observed here, suggests that the differences are not caused by a systematic error.

The best correlation (within 5% difference) between OND and DNS is observed for Na<sup>+</sup>, Ba<sup>2+</sup> and Mg<sup>2+</sup>. For Cl<sup>-</sup>, no trend is identified. Acid treatments (addition of HCl to the injected water) are routinely performed to remove solid CaCO<sub>3</sub> forming in the wells. This introduces occasional sample events containing a high concentration of Cl<sup>-</sup>, which may cause the high Cl<sup>-</sup> concentrations in DNS.



**Figure 5.2:** Comparison of experimental results (DHRTC New Samples) and reported results (Operator New Data) for similar samples: Parity plots illustrating the trend between the average of the reported concentrations in Operator New Data (OND) and the measured value from DHRTC New Samples (DNS). The solid lines represents the  $\pm 25\%$  deviation from a one-to-one correlation, which is marked by the dotted line.

Consider the trendline slopes, the best agreement between between OND and DNS is, surprisingly, observed for  $Ba^{2+}$ . However, in this trend 31% of the points are missing, as one points was excluded from the trend and 9 of the reported data points (OND) are missing.
lon	Linear trendline	Regression coefficient	Number of points
	ax + b	$R^2$	excluded in the trend
	mg/L		
Na <sup>+</sup>	0.9504 x + 464.78	0.7236	0 (-)
K+	1.1933 x - 14.88	0.8365	5 (16%)
$Ca^{2+}$	1.2212 x - 216.25	0.8848	0 (-)
Mg <sup>2+</sup>	1.0455 x + 2.1904	0.9433	5 (16%)
Sr <sup>2+</sup>	0.9168 x + 5.3133	0.9224	6 (19%)
Ba <sup>2+</sup>	1.0029 x + 0.9448	0.9517	1 (+ 9 missing, 31%)
CI-	No tren	d observed	-
$ $ SO $_4^{2-}$	1.1816 x - 78.405	0.9636	16 (50%)

**Table 5.1:** Comparison of experimental measurements of DHRTC New Samples (DNS) with the calculated average from Operator New Data (OND = x): Linear trendline equations and their regression coefficients for the parity plots shown in Figure 5.2.

### Inter-instrumental test

Four of the cations; Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>, were analysed with both IC and ICP-OES at DHRTC. The included sample set counts 61 samples. The parity plot comparing the concentrations determined with the two different instruments are given in Figure 5.3, with the linear trendlines and their regression coefficients given in Table 5.2.

The slope of the linear trendline is 1.0742, 0.9563, 0.943 and 0.7068 for Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>, respectively. Na<sup>+</sup> is the only ion for which the concentration determined using IC is higher than that determined using ICP-OES. The worst agreement between instruments is found for Ca<sup>2+</sup>; here the difference is 29%. For the remaining cations, the two methods agree within a difference of 7%, which is acceptable.

lon	Linear trendline	Regression coefficient	Number of points
	ax + b	$R^2$	excluded in the trend
	mg/L		
Na <sup>+</sup>	1.0742 x - 335.07	0.8178	2 (3%)
K+	0.9563 x - 4.1115	0.9228	6 (10%)
$Ca^{2+}$	0.7068 x + 156.3	0.9372	6 (10%)
$Mg^{2+}$	0.943 x - 9.2997	0.9672	7 (11%)

**Table 5.2:** Inter-instrumental test [IC vs. ICP-OES (x)]: Linear trendline equations and their regression coefficients for the parity plots shown in Figure 5.3.



**Figure 5.3:** Inter-instrumental test (IC vs. ICP-OES): Parity plots. The solid lines represents the  $\pm 25\%$  deviation from a one-to-one correlation, which is marked by the dotted line.

### Inter-laboratory test

Another set of samples; Operator New Samples (ONS), 71 in total, have been analysed with IC both at DHRTC (DNS) and by the operator (OND). The included ions are; Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. Sr<sup>2+</sup> and Ba<sup>2+</sup> were not detected using IC at DHRTC. It is noted, that the analysis at the operator's laboratory was done approximately one month after the samples were collected off-shore, whereas the analysis at DHRTC was carried out approximately one year after the samples were collected, because the samples were not available any time sooner.

Figure 5.4 displays the parity plots comparing the determined compositions and the linear trendlines and regression coefficients are given in Table 5.3.

All ions, but Na<sup>+</sup> show trends with slopes lower than one, meaning that the concentration determined at DHRTC is lower than that determined by the operator. For Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> the agreement between laboratories is within 9% difference, which is acceptable.  $SO_4^{2-}$  shows a poorer agreement (slope = 0.87). As previously, no trend is observed for Cl<sup>-</sup>.



**Figure 5.4:** Inter-laboratory test [DHRTC vs. operator (all IC)]: Parity plots. The solid lines represents the  $\pm 25\%$  deviation from a one-to-one correlation, which is marked by the dotted line.

lon	Linear trendline	Regression coefficient	Number of points
	ax + b	$R^2$	excluded in the trend
	mg/L		
Na <sup>+</sup>	1.0947 x - 1130.1	0.7784	2 (3%)
<b>K</b> +	0.958 x + 16.98	0.9837	3 (5%)
Ca <sup>2+</sup>	0.9418 x - 33.009	0.9345	5 (8%)
$Mg^{2+}$	0.9449 x + 10.119	0.9872	4 (7%)
CI-	No tren	d observed	-
$SO_4^{2-}$	0.8682 x + 69.416	0.9829	16 (26%)

**Table 5.3:** Inter-laboratory test [DHRTC vs. operator (x), all IC]: Linear trendline equations and their regression coefficients for the parity plots shown in Figure 5.4.

## 5.3 Discussion of findings

Based on the full study, some guidelines for future analysis of produced water samples and similar samples are given. [Copied directly from manuscript A.2]

- The samples must be filtered prior to analysis to avoid contamination from suspended solids. This is especially relevant for ICP-based techniques.
- For a sensitive determination of Ba<sup>2+</sup>, ICP-OES is advised. This is found important for an accurate prediction of the scale formation risk.
- For the ICP-based analyses a NaCl matrix is needed in the calibration standards.

 The use of hydrochloric acid for sample preservation should be avoided if chlorine concentrations are of interest.

Scale has proven to be a noteworthy risk in many of the oil fields in the Danish North Sea, including the Halfdan field, which will affect the lifetime of and production from a field. [107] Some of these commonly observed scales include SrSO<sub>4</sub> and BaSO<sub>4</sub>. These are both insoluble and especially critical when formed in the wellbore area. [107] The ionic composition of nine samples (DNS) has been subject to scale prediction calculations using the ScaleCERE program. The samples were chosen to represent the extremes in the total sample set; both high and low considering  $Sr^{2+}$ ,  $Ba^{2+}$  and  $SO_4^{2-}$ . The full output of this study is reported in the attached manuscript A.2. From the calculations, it was found that BaSO<sub>4</sub> is supersaturated in all samples at ambient and cool storage conditions. At reservoir conditions, which is where the formation is most critical, all samples but those with the lowest concentrations (Ba<sup>2+</sup> < 0.8 mg/L and low SO<sub>4</sub><sup>2-</sup> < 200 mg/L) are supersaturated. This proves that BaSO<sub>4</sub> is a serious threat in most wells, especially where water flooding is applied. SrSO<sub>4</sub> is found to be supersaturated only in the samples with a SO<sub>4</sub><sup>2-</sup> concentration higher than 1000 mg/L. Again, care must be taken at the wells where water is injected as the injection water often introduces high amounts of SO<sub>4</sub><sup>2-</sup> ( $\approx$  2700 mg/L). Figure 5.5 summarizes these findings.



**Figure 5.5:** Map of the Halfdan field. From Danish Energy Agency. [15] Information on scale observations and predictions has been added by the authors. The information is based on observations reported by the field operator (observations) combined with results found in the work presented here (predictions).

# 6 Study 2, part 2: Produced water from the North Sea – A case study and analytical guidelines. Part 2: Impact of storage

## 6.1 Short introduction

Part 1 presented a new analytical workflow for the sample preparation and analysis of produced water samples from the Danish North Sea covering the ions: Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. Routine IC analysis was combined with ICP-OES. Part of the samples included in this study had been stored up to one year prior to the analysis. The samples were stored by the operator as the protocol dictates so. In many laboratories, samples are stored (also for periods more than one year) in case re-analysis or a new type of analysis is requested. Reliable results from analysis of "old" samples require that the samples are still representative for the time of sampling. The full study is presented and discussed in the attached manuscript A.3.

The samples included in this PhD are all produced water samples from off-shore oil producing platforms in the North Sea. The produced water mainly consists of formation water, which is a natural substance not only containing the already mentioned ions. For example, sulphate reducing bacteria are known to be present. [3, 48, 68] In addition, the samples are exposed to significantly changing conditions during sampling, transport, analysis and lastly storage. These together may cause compositional changes during storage. The latter because the samples get time to equilibrate thermodynamically.

The presented study aims to evaluate on the observed changes in the produced water chemistry (PWC). 61 samples from the Halfdan field are included as a case study, these are referred to as DHTC New Samples (DNS). They are all collected from wells distributed across the entire field and were collected from June 2018 to March 2019 and with the new, revised sampling protocol described in the attached manuscript A.2. The samples were analyzed twice: At the time of arrival to the laboratory, and one year later - following the exact same analytical procedure. The samples were stored in well-sealed blue cap bottles, in a dark refrigerator at  $5^{\circ}$ C to limit the effect of the above discussed possible influencing factors.

Parity plots are used to compare the experimental results from the two analyses. In the parity plots, the one-to-one correlation is shown together with the  $\pm 25\%$  deviations from this correlation. All measurements within the  $\pm 25\%$  deviations are included in the comparison and discussion.

## 6.2 Main findings

At a first glance , no visible precipitation, nor gas formation (for example  $H_2S$ ) is observed. However, this does not necessarily mean nothing has happened. The light smell of oil traces may hide the smell of  $H_2S$  (g); and precipitation can have occurred in amounts smaller than what is possible to be observe with the human eye.

The compostional changes determined analytically are shown in Figure 6.1 and the associated linear trendline equations and their regression coefficients are given in Table 6.1. According the comparison, all ions except  $Sr^{2+}$  and  $SO_4^{2-}$ , are depleted during the one year in storage. However, the linear trendline slopes are  $\geq 0.94$  for Na<sup>+</sup>, Mg<sup>2+</sup> and Ba<sup>2+</sup>, which suggests that no significant changes have occurred. On the contrary, the slopes for K<sup>+</sup> and Ca<sup>2+</sup> are 0.81 and 0.66, respectively. These are notable and suggest that a change has occurred. A first assumption is that elements have precipitated as chloride salts; but the decrease in the two cations cannot be correlated with a decrease in the Cl<sup>-</sup> concentration, thus, this is not the explanation. Instead, we argue the observed decrease in the Ca<sup>2+</sup> concentration is due to formation of solid CaCO<sub>3</sub> as the samples equilibrate with the atmospheric CO<sub>2</sub> (g).

No consistent trend is observed for Cl<sup>-</sup>. The concentrations of  $SO_4^{2-}$  are found to be unaffected by the storage. It is argued that the excluded  $SO_4^{2-}$  points represent erroneous measurements in 2018/2019 (see Manuscript A.2 for details).

lon	Linear trendline	Regression coefficient	Number of points
	ax + b	$R^2$	excluded in the trend
	mg/L		
Na <sup>+</sup>	0.9618 x + 1276.5	0.8160	2 (3%)
K+	0.8101 x + 29.271	0.8087	10 (17%)
Ca <sup>2+</sup>	0.6648 x + 256.06	0.8861	12 (10%)
Mg <sup>2+</sup>	0.9671 x + 7.4439	0.9585	9 (10%)
Sr <sup>2+</sup>	1.0532 x - 0.0629	0.8621	5 (8%)
<b>Ba</b> <sup>2+</sup>	0.9368 x + 0.0237	0.9832	9 (15%)
CI-	No regular	trend observed	-
$SO_4^{2-}$	1.0220 x - 16.111	0.9691	29 (48%)

**Table 6.1:** Effect of one year storage of produced water samples: Linear trendline equations and their regression coefficients for the parity plots shown in Figure 6.1. The value measured first (2018/2019) is taken as reference (x).



2018/2019 measurement, mg/L

**Figure 6.1:** Parity plots illustrating the change in sample composition [DHRTC New Samples (DNS) and TOTAL New Samples (TNS)] after one year of being stored. The solid lines represents the  $\pm 25\%$  deviation from a one-to-one correlation, which is marked by the dotted line.

## 6.3 Discussion of findings

The time of storage is found to cause only minor changes in the sample compositions with respect to the major inorganic ions. The concentrations of most ions (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and Ba<sup>2+</sup>) are found to decrease. The determined changes are significant for K<sup>+</sup> and Ca<sup>2+</sup>. It is, thus, suggested that the produced water samples are analyzed as soon as possible after sampling to limit the impact of storage. However - and importantly - the findings show that the samples do retain most of their value despite storage and can be stored in case of later need of analysis.

The included samples have not been preserved after sampling. Normally, HCl and/or HNO<sub>3</sub> is added to the produced water to limit microbial activity (sulphate reducing bacteria). The comparison presented here suggests no significant changes in the  $SO_4^{2-}$  concentrations, thus, questioning the need for preservation. However, preservation may have other reasons and may still be advantageous. If so, one must be aware of *why* and, consequently, *how* preservation is done.

# 7 Study 3: Analysis of heavy metals in produced water

## 7.1 Introduction

A study of heavy metals are included in this project to evaluate on the potential presence of such; and consequently, their impact on the (eco)toxicology of the produced water. [25, 49, 91, 111] A published study from Brazil reports observations of heavy metals in toxic levels in the produced water, thus, underlining the importance of a similar study on produced water from the Danish North Sea. [111] The typical detection limit of an ICP-OES is mg/L (ppm = 1000 ppb), whereas it is ng/L (ppt = 0.001 ppb) for common ICP-MS instruments. For this reason, ICP-MS is widely used for the analysis of (heavy) metals in trace amounts. [24, 25, 91, 103] The present study covers  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ,  $Hg^{2+}$  and  $Pb^{2+}$ .  $Mg^{2+}$ ,  $Ba^{2+}$  and  $Sr^{2+}$  are mainly included to function as cross-check with the results achieved using ICP-OES. The author is aware that  $Mg^{2+}$ ,  $Ba^{2+}$ ,  $Sr^{2+}$ , and  $Mn^{2+}$  are not by definition heavy metals, but for the ease of the reader all metals are referred to as heavy metals in this chapter.

The main challenge for the application of ICP-MS in this study is the high-salinity nature of the produced water samples. The total dissolved solids (TDS) may reach 40% in the samples included in this study. The involved risks include: 1) Ion suppression caused by a high concentration of easily ionized elements like Na<sup>+</sup> and K<sup>+</sup>, and 2) spectral interference caused by polyatomic atoms due the high levels of eg. Na<sup>+</sup>, Cl<sup>-</sup>, K<sup>+</sup> and Ca<sup>2+</sup>. [24] Most standard methods for ICP-MS, including ISO (International Organization for Standardization) standards, define a maximum limit of 0.2% TDS in the samples, corresponding to 2000 ppm. [24, 40, 41] Therefore, most heavy metal analysis in high-salinity samples using ICP-MS include extensive sample pre-treatment, like analyte separation or pre-concentration. [25, 108, 118] To avoid this, the primary goal is to improve the matrix tolerance. Aerosol dilution allows this. The pump delivers sample solution at a normal uptake rate to the nebulizer, but a diluent gas flow (argon) is introduced between the ICP-MS spray chamber and the torch. Consequently, the aerosols are diluted before they enter the torch. [24] Aerosol dilution reduces the plasma loading, which leaves more energy for matrix decomposition and analyte ionization, thus reducing ionization suppression. To apply aerosol dilution, the instrument is run in high-matrix introduction (HMI) mode.

### 7.1.1 Approaching the experiment

From the literature, expected concentrations of the included metals in produced water are identified. A study of produced water from the Gulf of Mexico reports concentrations in the range of <0.1 to 28  $\mu$ g/L, including Hg<sup>2+</sup>, Ni<sup>2+</sup> and Pb<sup>2+</sup>. [47] A study from Brazil reports Mn<sup>2+</sup> concentrations in produced water in the range of 19 - 35  $\mu$ g/L. [91] Another Brazilian study covers the analysis of ten heavy metals using ICP-MS (combined with on-line analyte separation/preconcentrations). Of the ten metals, four are included in the present study. The observed concentrations of these are; Pb<sup>2+</sup>: 0.06 - 1.5  $\mu$ g/L, Ni<sup>2+</sup>: 0.2 - 5.5  $\mu$ g/L, Zn<sup>2+</sup>: 0.3 - 3400  $\mu$ g/L, and Mn<sup>2+</sup>: 4.2 - 6200  $\mu$ g/L. [25] Based on these concentrations, the instrument was calibrated in the range of 0.1  $\mu$ g/L to 1000  $\mu$ g/L for

all included metals. Samples with concentrations above these can be identified from the initial analyses and diluted to match the calibration range.

In the optimization of the experiment,  $Mg^{2+}$ ,  $Sr^{2+}$  and  $Ba^{2+}$  are excluded as these elements are present in the samples at levels >1000 times higher than the remaining metals included except  $Ba^{2+}$ , which in some samples is expected to be present at ppb-level.

### 7.1.2 Samples

The samples included in this study are sampled using the new revised sampling protocol described in Section 3.1.3. Table 7.1 lists the samples included in the study on heavy metals and their sampling location. The samples from the Halfdan field have been specified further, with the field area from which they originate: North East (NE), North West (NW), South East (SE) and South West (SW).

Field		Number of samples
Dan		9
Kraka		7
Valdemar		8
Halfdan	Total	31
	NE	8
	NW	6
	SE	13
	SW	4

**Table 7.1:** List of samples included in the analysis of heavy metals using ICP-MS. The samples from the Halfdan field are further divided into the areas from which that originate: North East (NE), North West (NW), South East (SE) and South West (SW).

## 7.2 Experimental results

### 7.2.1 Calibrations

The first run includes samples number 1-34 (Run 01). The details of these samples are given in Table B.13, see Appendix B. The samples are run undiluted and the calibration solutions are prepared in pure 2% HNO<sub>3</sub>. The calibration curves are shown in Figure 7.1.

For most of the elements, linear calibration curves are observed in both "No gas" and "He" mode. However,  $Mg^{2+}$ ,  $Sr^{2+}$  and  $Pb^{2+}$  shows curved calibration curves at low concentrations (<100 ppb) in "No gas" mode. In "He" mode,  $Hg^{2+}$  shows curvature at low concentrations (<10 ppb) and the remaining ions show linear calibrations in the full range. The calibration regressions are given in Table 7.2. For all calibrations, the regression is 0.9968 (Pb<sup>2+</sup>) or higher.

For the second run (Run 02), which covers samples number 35-55, the calibrations solutions are prepared using synthetic seawater as the solvent. Again, the samples were run undiluted. The calibration curves are shown in Figure 7.2 and the calibration regressions are given in Table 7.2. The concentrations of  $Mg^{2+}$  in the samples are way beyond the range at which an acceptable accuracy is achieved (discussed in Section 7.2.3), thus,  $Mg^{2+}$  is left out of the analysis going forward.

Across all elements, the measured intensity decreases upon the change from calibration solutions prepared in pure 2% HNO<sub>3</sub> to synthetic seawater. This is as expected, and proves the significance of ionization suppression caused by the background matrix. This also underlines the importance of matrix match between calibration solutions and samples.



**Figure 7.1:** Calibration for Run 01 on the ICP-MS. The calibration curves are prepared in a pure 2% HNO<sub>3</sub>. The right curves show a zoom of the left curves.

As in Run 01, we find linear calibration curves for  $Hg^{2+}$ ,  $Ba^{2+}$  and  $Pb^{2+}$  in "No gas" mode. Mn<sup>2+</sup> and Sr<sup>2+</sup> shows curvature at low concentrations (<100 ppb). In "He" mode, all analytes, but Sr<sup>2+</sup> show linear calibration curves. For all elements, the calibration regressions are higher (closer to one) for the calibrations prepared in synthetic seawater than those prepared in 2% HNO<sub>3</sub>. This confirms the need for a matrix match of the calibration solutions, i.e. synthetic seawater as used in Run 02.



Concentration in standard, ppb

Figure 7.2: Calibration for Run 02 on the ICP-MS. The calibration curves are prepared in a synthetic seawater water.

	-			
Element	An	alytical ru	in and mod	е
	Run	01	Run	02
	"No gas"	"He"	"No gas"	"He"
$Mg^{2+}$	0.9977	1.00	-	-
$Sr^{2+}$	0.9974	1.00	-	0.9999
$Ba^{2+}$	0.9977	1.00	0.9999	0.9996
Mn <sup>2+</sup>	0.997	0.9999	0.9997	0.9999
$Hg^{2+}$	0.9975	1.00	1.00	0.9991
$Pb^{2+}$	0.9968	1.00	1.00	0.9991
Zn <sup>2+</sup>	-	1.00	-	0.9999
$As^{2+}$	-	1.00	-	0.9999

Table 7.2: Calibration regressions for the calibration curves displayed in Figures 7.1 and 7.2.

From the presented calibration curves, we argue that "He" mode will provide good results for all analytes but  $Hg^{2+}$  within the calibration range. For  $Hg^{2+}$ , "No gas" mode performs slightly better. This is confirmed by the calibration regressions (Hg: 1.00 in "No gas" and 0.9991 in "He" mode).

### 7.2.2 Comparison with ICP-OES results

Mg<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> have also been analysed using the ICP-OES. Thus, an inter-instrumental (and inter-laboratory) quality check of the concentrations in the samples is made possible. Figures 7.3 and 7.4 shows parity plots for the comparison of the results obtained using ICP-OES and ICP-MS, respectively. The linear trendlines and their regression coefficients for the parity plots are given in Table 8.1.

From Figure 7.3, it is seen that the concentration of  $Mg^{2+}$  in the samples determined with ICP-MS (Run 01) is significantly higher than that determined using the ICP-OES; the correlation coefficient (slope of the trendline, a) is 0.20 and 0.47 in "No gas" and "He" mode, respectively. This suggests that the  $Mg^{2+}$  concentration is overestimated using ICP-MS, most likely caused by the fact that the concentrations of  $Mg^{2+}$  are much higher (200-800-fold) than the highest calibration standard. Dilution could solve this, but there is no need as the real purpose of the ICP-MS analysis is the quantification of the heavy metals. Going forward,  $Mg^{2+}$  is excluded from the ICP-MS analysis. For both  $Sr^{2+}$  and  $Ba^{2+}$ , the best agreement between the ICP-OES and ICP-MS analyses are found using "He" mode.



Figure 7.3: Parity plots for the comparison of the results achieved from analysis using ICP-OES and ICP-MS,

respectively. Run 01.

In Run 02, good agreement between ICP-OES and ICP-MS is observed for both  $Sr^{2+}$  and  $Ba^{2+}$ , as shown in Figure 7.4. The slope of the linear trendlines, given in Table 7.3, are 1.01 and 1.06 for  $Sr^{2+}$  and 1.03 and 1.04 for  $Ba^{2+}$ , in "No gas" and "He" mode, respectively. That is, the slopes are slightly closer to one in "No gas" mode than "He" mode. The regression coefficients are slightly closer to one in "He" mode. In conclusion, the two modes perform similarly.



Concentration measured by ICP-MS, ppb

**Figure 7.4:** Parity plots for the comparison of the results achieved from analysis using ICP-OES and ICP-MS, respectively. Run 02.

It is found that the correlation between the ICP-OES and ICP-MS analyses are much better for Run 02 than Run 01, suggesting that the calibration solutions prepared in synthetic seawater are superior to the calibration solutions prepared in 2% HNO<sub>3</sub>.

It is noted that the ICP-MS is only calibrated up to 1000 ppb, thus, the concentration of mainly  $Sr^{2+}$ , but also  $Ba^{2+}$ , exceeds this for most samples. However, the performance is still good, which is indicated as agreement with the concentrations determined using the ICP-OES.

Element		Linear regression	Regression coefficient
		ax + b	$R^2$
Run 01			
	Mg [No gas]	0.2013 x + 27037	0.5543
	Mg [He]	0.4662 x + 53922	0.5674
	Sr [No gas]	0.6483 x + 47241	0.5800
	Sr [He]	0.7473 x + 45772	0.6036
	Ba [No gas]	0.8798 x + 424.78	0.9553
	Ba [He]	1.0654 x + 392.25	0.9545
Run 02			
	Sr [No gas]	1.0103 x + 19392	0.9560
	Sr [He]	1.0616 x + 7798.2	0.9642
	Ba [No gas]	1.0278 x - 0.5747	0.9974
	Ba [He]	1.042 x + 24.139	0.9992

**Table 7.3:** Comparison of concentrations determined using ICP-OES (x) and ICP-MS: Linear trendlines and regression coefficients for the parity plots shown in Figures 7.3 and 7.4.

### 7.2.3 Composition of samples

The measured concentrations of the (heavy) metals in the samples are given in Figure 7.5. For all metals, the concentrations determined in both "No gas" and "He" mode are given for full transparency. Generally, the determined concentrations are similar independent on the mode. However, it is noted, that the analytical workflow is very preliminary; the calibration curve for samples 1-34 (Run 01) are prepared in pure 2% HNO<sub>3</sub> and none of the samples were diluted prior to the analysis. The latter shows to be relevant especially for the analysis of Sr<sup>2+</sup> and Ba<sup>2+</sup>. Fortunately, for most samples, the determined concentrations are within the calibration range for the remaining analytes:  $Mn^{2+}$ ,  $Pb^{2+}$ ,  $Hg^{2+}$ ,  $Zn^{2+}$  and  $As^{2+}$ . Considering "He" mode, only one sample is beyond the calibration range for Pb<sup>2+</sup> and Zn<sup>2+</sup>.



**Figure 7.5:** Determined concentrations of analytes in the samples. Notice that samples 1-34 are analysed in Run 01, where the calibration solutions are prepared in pure 2% HNO<sub>3</sub>, and samples 35-55 are analysed in Run 02, where the calibration solutions are prepared in synthetic seawater. The numbers given before the element symbol indicates the m/z charge value at which the metal has been detected.

In Figure 7.5, it is found that  $Mn^{2+}$  is present in levels between a few ppb to 500 ppb in most samples; in 6 of the samples (10%), the  $Mn^{2+}$  concentration is significantly larger. The samples with  $[Mn^{2+}]>500$  ppb all originate from the Kraka field. Significant for both  $Zn^{2+}$  and  $Pb^{2+}$  is that they are found to be present at measurable concentrations in very few samples, but that in these samples, the measured concentrations are extremely high: Up to 6500 ppb for  $Zn^{2+}$  and 200 ppb for  $Pb^{2+}$ . A similar observation is reported by Oliveira *et al.* [25] The samples with high  $Pb^{2+}$  and  $Zn^{2+}$  concentration are all collected at the Valdemar field.  $Hg^{2+}$  is detected at concentrations below 5 ppb in most samples. The samples showing the highest concentrations of  $Hg^{2+}$  are collected at the Halfdan field; but this trend is not strong. Lastly, the samples showing the highest levels of  $As^{2+}$ 

are collected at the Halfdan field. The observed regional differences are illustrated in Figure 7.6.



**Figure 7.6:** Map showing where heavy metals have been detected at significant levels in the produced water. The metals given in parentheses are observed only in one sample from the respective field.

A study by Trefry *et al.* presents results indicating that the concentration of heavy metals is positively correlated to total dissolved solids (TDS). [47] Figure 7.7 shows a plot of the sum of concentrations of the eight major inorganic ions (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) versus the sum of concentrations of the included heavy metals (Mn<sup>2+</sup>, Pb<sup>2+</sup>, Hg<sup>2+</sup>, Zn<sup>2+</sup> and As<sup>2+</sup>). The plot does not confirm the results presented by Trefry *et al.* 



Figure 7.7: Sum of inorganic ions (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) versus the sum of the included heavy metals (Mn<sup>2+</sup>, Pb<sup>2+</sup>, Hg<sup>2+</sup>, Zn<sup>2+</sup> and As<sup>2+</sup>).

## 7.3 Discussion of findings

Significantly high concentrations of the included heavy metals are observed in some samples. Besides the use for water type classification, the quantification of heavy metals provide valuable input for planning of cleaning procedures prior to discharge of produced water. In the Danish North Sea, the cleaning procedures mainly focus on the removal of dispersed oil. Therefore, a mapping of heavy metals may be valuable for further optimization of the claning procedures. The author stresses that the concentrations reported in this study are identified in produced water samples. Cleaned water intended for discharge was not made available for the study presented in this thesis. However, the concentrations in discharge water are most certainly lower than those reported here. A Chinese study presents results showing a cleaning procedure can be very effective, also regarding heavy metals. [49]

A Norwegian study from 2013 by Bakke *et al.* presents evidence that the discharge of produced water has local effects, and that these effects are confined within 1-2 km of the outlet. [103] This limits the harmful effects of produced water discharge significantly. However, it does not make them indifferent. Furthermore, the study by Bakke *et al.* underlines that cumulative effects may have significant effects. Trefry *et al.* studied the bioaccumulation of heavy metals from discharged produced water in different aquatic organisms and found that especially  $Ba^{2+}$  (and  $Fe^{2+}$ ) was enriched with time. [47] Additionally, their findings suggest a potential bioaccumulation of  $Hg^{2+}$  and  $Pb^{2+}$ . This underlines the importance of including the heavy metals in a characterisation of the produced water types.

Figure 7.6 shows that different heavy metals (in significant concentrations) have been identified at different fields. Thus, regional variations are observed. Unique to the Valdemar field is the observation of significant levels of  $Pb^{2+}$  and  $Zn^{2+}$ . At the Halfdan field, significant levels of  $As^{2+}$  are observed; and at the Kraka field, high levels of  $Mn^{2+}$  are observed. These heavy metals are not expected to be introduced to the wells by completion fluids or production chemicals. Therefore, the observed differences are most likely caused by a natural variance. Thus, the identification of (unique) heavy metals can be included in the produced water signature - as that classified in Paper 1 with the end-members.

### 7.3.1 Work going forward

The presented results are found to be valuable as a starting point for taking the study of heavy metals in produced water from the Danish North Sea further. Also, the results proves that there is a need for paying attention to heavy metals during the cleaning procedures of produced water prior to discharge. As a next step, all samples should be re-analysed, with the calibration curve prepared in synthetic seawater, and the samples should be run both undiluted and 100-fold diluted. Secondly, the choice of internal standard (IS) may be changed; the current ISs are selected to match the m/z-value of the analytes. Alternatively, the ISs could be chosen to the match ionization energies. Ideally, certified reference material is used as quality control. Also, inclusion of cleaned produced water intended for discharge will provide a realistic picture of what is disposed - and whether the current cleaning procedure is as effective as needed.

To extend the current study, more samples from the fields included in this study must be analysed. Preferably, also including samples from the Dan field to study if Halfdan S. and Dan still compose the same water type when heavy metals are included. The results from the ICP-MS analysis can then by added to a PCA similar to that presented in Study 1. Kraka is found (Study 4) to contain high levels of  $Mn^{2+}$  - and the field is known to produce high saline water. The Valdemar field is found to contain several of the heavy metals ( $Mn^{2+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$  and  $As^{2+}$ ) in significant levels. In Study 2, it was shown that the water produced at the Valdemar field also contains high levels of  $Ba^{2+}$  compared to the other fields included in this thesis. It is suspected, that these two (high levels of heavy metals and  $Ba^{2+}$ ) correlate. In conclusion, it is expected that a correlation between the identified end members and the level of heavy metals can be identified. Further, a mapping of the heavy metals may add information to the understanding of flow patterns.

# 8 Study 4: Non-target screening of organic compounds in produced water samples

## 8.1 Short introduction

Produced water is the largest by-product of the oil and gas industry. In the Danish North Sea, the produced water is currently discharged into the sea. The OSPAR Convention, which was set in to force in 1998, regulates the requirements for discharge water; a discharge limit of 30 mg of dispersed oil per liter of water is set as an annual average, but there is no limit on dissolved species. [76] It is largely unknown to what extent the hydrocarbons will dissolve in the produced water. Therefore, we argue dissolved species may be important to characterise. Additionally, crude oil contains a small fraction of organic polar species which will partition into the aqueous phase. These species will most certainly contribute to the overall composition of the produced water. Therefore, effort to identify - and ultimate quantify these species - are required to fully characterise the produced water. Further, this information adds information to employ regulations and efficient depollution strategies that cover the full composition of the produced water.

### Experimental

Non-discriminative liquid-liquid extraction (LLE) is combined with comprehensive twodimensional gas chromatography (GC×GC) coupled to a high-resolution mass spectrometer (-HRMS) for tentative identification of dissolved organic species in produced water. Nine samples, all from the Halfdan field and sampled in winter 2018/2019, were included in the present study. The samples were collected from four different wells, that were chosen to cover as much of the Halfdan field as possible. Table 8.1 provides more detailed information on the samples.

Well area*	Number of samples	Distribution in time
NC	2	3 months
SE	2	3 months
SE	2	3 months
NE	3**	4 months

 Table 8.1:
 Details on the included samples for the GCxGC-HRMS analysis. \*Field areas are shown in

 Chapter 4, Figure 4.5. \*\*Two of the samples have been collected at the same day (and from the same well).

As a final step in the sample preparation, the samples were derivatized using BTSFA+TMCS [N,O-Bis(trimethylsilyI)trifluoroacetamide+trimethylchlorosilane]. All samples were prepared and analysed in triplicates. GC Image v2.8.3 was used for peak detection and library search. [119] The achieved mass spectra were matched against the NIST Mass Spectral Library with a minimum match factor of 700. [75] Jonas F. Sundberg created a data processing pipeline in Python, which was used to sort and reduce the extensive data. [85] The full study is presented and discussed in a manuscript, that has not yet been

approved for publication by the operator.

## 8.2 Main findings

### Sample preparation: Recovery

A synthetic produced water containing six representative model compounds (benzoic acid, phenol, 2-naphthoic acid, cyclohexanecarboxylic acid, and octanoic acid) in simulated formation water was prepared to evaluate the variability in the sample preparation protocol and potential instrumental analysis. Each of the model compounds were present at 5 ppm, thus, reaching a total organics concentration of 30 ppm in the synthetic seawater. The synthetic water was extracted six times in two batches. Three procedural blanks were prepared to determine the background levels and experimental sources of contamination. The recovery was determined based on peak volumes with comparison to pure standards. These were found to vary between from 35% (benzoic acid) up to 89% (phenol). Considering the multi-step sample extraction procedure, which also includes a derivatization reaction, this is acceptable. The protocol was found to be reproducible.

### Chromatographic separation

The considerations behind the choice of columns are described in Section 3.5.2. The goal was to separate saturated and aromatic polar species. This was achieved as shown in Figure 8.1.



Boiling point

**Figure 8.1:** Representative 2D-chromatogram. The lower circle approximately marks the region of saturated acids and the upper region shows the aromatic acids.

### **Identified compounds**

Approximately 1500 features were detected in each sample. This was narrowed down by an implementation of a data processing pipeline. This sorts, organizes and make senses of the achieved information. Features with a match factor below 700 is considered poor,

and therefore, removed from the results. Additional two factors were included to increase confidence in the identified species; retention index (Kovats) and the presence of the molecular ion. Furthermore, only features that were present in all three replicates were included in the final feature table - and all compound duplicates were removed as isotopes are not of interest in this study.

The applied data processing pipeline reduced the number of features from approximately 1) 1500 (detected) features to 2) 200 (library hits, match factor > 700), to a final of 3) 50 - 70 compounds (with duplicates based on name removed). Out of these, 15 compounds were present in all nine samples. These are listed in Table 8.2.

Two of the detected dissolved species are alcohols and the remaining are saturated or aromatic acids. This is as expected, as these have polarities allowing them to dissolve in water (as opposed to, i.e. hydrocarbons).

## 8.3 Discussion of findings

Currently, studies on dissolved organic species in produced water are few as the analysis is challenging. Here, we present a successful analytical workflow for this. The presented method is only qualitative, thus, more work is required to develop a fully qualitative *and* quantitative analytical workflow. However, the presented workflow is an important first step on the path to the development of such method. As expected, the identified compounds are alcohols and acids, as the slight polar nature of these species allow them to easier dissolve into the water phase - as oppose to their parent hydrocarbons.

The organic content in produced water has been shown to correlate to the salinity, which is most likely caused by a salting-out effect. [106, 104, 105, 94, 65]. Carothers and Kharaka published the first paper on organic acids in produced water in 1978. [115]. They presented a study of produced water from across the Norwegian shelf, from which they found that the organic acid concentrations have a strong positive correlation with alkalinity and a weak positive correlation with pressure. This is later confirmed by several studies. [106, 104, 105] These studies also suggest that the organic acids may act as buffers in the water system, which affects the diegenises processes in the reservoirs. [106, 104, 105] The samples included in the study presented in this thesis do not cover wells with water types showing significantly different salinites. Therefore, the proposed correlation cannot be studied. Furthermore, the included study is not quantitative.

### Work going forward

The study presented here only includes organic species identified in all included samples. A next step is to identify compounds that are unique for one well or field area. This will add to a regional characterisation as that presented in Chapter 4. The needed data (chromatograms) for the nine included samples exists but has not been analysed yet.

Ideally, more samples representing the different water types characterised in Study 1 are to be included. This will allow for an even more detailed study of the link between the water types and the dissolved organic species.

Identified compound	MS-ready	Formula	Mol. Weight	XlogP	SMILES	Classification
3,4-Dimethylbenzoic acid, TMS derivative	3,4-dimethylbenzoic acid	C9H10O2	150.17	2.7	CC1=C(C=C(C=C1)C(=0)O)C	Aromatic acid
Heptanoic acid, TMS derivative	heptanoic acid	C7H14O2	130.18	2.5	CCCCCCC(=0)0	Saturated acid
3-Methyl-1-cyclohexanecarboxylic acid,	3-methylcyclohexane-1-carboxylic acid	C8H14O2	142.2	2.1	CC1CCCC(C1)C(=0)O	Saturated acid
unneuryisiiyi ester (stereoisonner 2) 4 Noobthaia aaid TMC dariivatiiva	and the second contraction and the second		170 10	, ,	$\bigcirc(\bigcirc -)\bigcirc(\bigcirc -)\bigcirc(-)\bigcirc(-)\bigcirc(-)\bigcirc(-)\bigcirc(-)\bigcirc(-)\bigcirc(-)\bigcirc(-)\bigcirc(-)\bigcirc($	Aromotic acid
I-Napriliouc acia, TIVIS URIVALIVE	парпиланеле- I -сагрохулс асю		1/2.10	 0	O(D=)	Alomatic acid
Nonanoic acid, TMS derivative	nonanoic acid	C9H18O2	158.24	3.5	cccccccc(=0)0	Saturated acid
$(\pm)$ -2-Phenylpropanoic Acid,	2-phenylpropanoic acid	C9H10O2	150.17	1.9	CC(C1=CC=CC=C1)C(=0)0	Aromatic acid
trimethylsilyl ester						
Octanoic acid, TMS derivative	octanoic acid	C8H16O2	144.21	ი	CCCCCCCC(=0)0	Saturated acid
1-Hexadecanol, TMS derivative	hexadecan-1-ol	C16H34O	242.44	7.3	CCCCCCCCCCCCCCC	Saturated alcohol
Cyclohexaneacetic acid, TMS derivative	2-cyclohexylacetic acid	C8H14O2	142.2	2.5	C1CCC(CC1)CC(=0)0	Saturated acid
Trimethylsilyl 2,3-dimethylbenzoate	2,3-dimethylbenzoic acid	C9H10O2	150.17	2.8	CC1=C(C(=CC=C1)C(=0)0)C	Aromatic acid
3-Methylbutanoic acid, TMS derivative	3-methylbutanoic acid	C5H10O2	102.13	1.2	CC(C)CC(=0)0	Saturated acid
Trimethylsilyl 4-propylbenzoate	4-propylbenzoic acid	C10H12O2	164.2	3.4	CCCC1=CC=C(C=C1)C(=O)O	Aromatic acid
Cyclohexanecarboxylic acid, TMS derivative	cyclohexanecarboxylic acid	C7H12O2	128.17	1.9	C1CCC(CC1)C(=0)0	Saturated acid
Cyclopentylcarboxylic acid, TMS derivative	cyclopentanecarboxylic acid	C6H10O2	114.14	1.3	C1CCC(C1)C(=0)O	Saturated acid
4-tert-Butylphenol, TMS derivative	4-tert-butylphenol	C10H14O	150.22	3.3	CC(C)(C)C1=CC=C(C=C1)O	Aromatic alcohol

Table 8.2: List of compounds detected in all nine samples. The MS-ready name corresponds to the non-derivatized parent, on which the properties are based. XlogP values were obtained from the PubChem database.

# 9 Thesis summary

The presented work covers the produced water chemistry (PWC) of four fields in the Danish North Sea: Dan, Halfdan, Kraka and Valdemar. From a production perspective, the attention on PWC historically has been focused on the inorganic ions: Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. The presented thesis expands on this and includes the heavy metal ions: Mn<sup>2+</sup>, Pb<sup>2+</sup>, Hg<sup>2+</sup>, Zn<sup>2+</sup> and As<sup>2+</sup>. In addition, a complementary study of the dissolved organic species on a subset of the samples is presented.

Based on historical data on the inorganic ions mentioned above, Study 1 (Paper A.1) classifies five end-members, which differ in the produced water composition. It was found that each of the four fields have their own characteristics; and the Halfdan field display two types of produced water. The water types mainly differ in total salinity (highly governed by Na<sup>+</sup> and Cl<sup>-</sup>), and the concentrations of SO $_4^{2-}$  and Ba $^{2+}$ , respectively. The most saline water is identified at the Kraka field, followed by Dan and Halfdan South. Also, these fields show the highest  $SO_4^{2-}$  concentrations (ten times higher than the Halfdan N. and Valdemar fields). For the Dan and Halfdan S. fields this is explained by the fact that these fields are water flooded. The Valdemar field shows significantly different - and much higher levels of Ba<sup>2+</sup> ( $\approx$ 45 mg/L) than the remaining fields ( $\approx$ 1 mg/L). The second highest level of Ba<sup>2+</sup> is found in the produced water from Halfdan N. ( $\approx$ 12 mg/L). The information on the  $Ba^{2+}$  (and  $Sr^{2+}$ ) concentration is extremely valuable for the prediction of hard scale formation. At the wells where scale is a severe risk, much caution much be paid if/when water injection is employed as production strategy: Often seawater is used as the injection fluid and this contains high concentrations of  $SO_4^{2-}$  (>2000 mg/L). The presented findings may be especially relevant for Halfdan North, where relatively high concentrations of  $Ba^{2+}$ is observed and water injection is employed. Additionally, the PWC and the variations in the classified end-members highlight that a "one size fits all" strategy for water injection most likely does not exist. Caused by the large variations in salinity, the resulting salinity gradient resulting from a mixing of the originally present (formation) water and the injection water will differ greatly between the fields. This will cause very different chemical and physical processes at the areas with different water types with potentially different recovery conditions as a result. Thus, the composition of the injection water may be optimized based on the classified end-member.

To determine the five end-members, principal component analysis (PCA) was applied. This approach proved to be ideal for the introduced analytical purpose. Outliers in the data were easily detected and excluded from the data. Furthermore, a clear distinction between the end-members was observed. From the data analysis, similarities in the water produced at the Dan field and the southern part of the Halfdan field were observed. We argue, this proves that the water produced at the two fields either 1) has the same origin, or 2) has migrated through the fields, which suggests the two fields are connected. This observation was supported by literature. This additional conclusion shows the diverse use , from production chemistry to pure geochemistry, of the classified end-members.

During the work presented in Study 1, see Paper in Appendix A.1, questions started to arise regarding the reliability of the historical data, which the study is based upon. Especially, the reported  $Ba^{2+}$  concentrations were called into question. For some samples

(4%), the information was missing. More significantly, the reported  $Ba^{2+}$  concentration was either 0 or 1 mg/L for 79% and 6.5%, respectively. It was found, that this has been common practice if the concentration was below the lower limit of detection for the analytical technique used by the operator. Considering the importance of an accurate  $Ba^{2+}$  determination for a scale prediction, a need for a more sensitive analytical workflow was identified. Therefore, inductively coupled plasma - optical emission spectroscopy (ICP-OES) was introduced.

The main challenge of an accurate analysis of the inorganic ions, and especially  $Ba^{2+}$ , in produced water is the high-salinity matrix, which is an inevitable condition of produced water. Study 2 (Appendix A.2) presents a new analytical workflow utilizing the benefits of ICP-OES for the sensitive analysis of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> in produced water. This is combined with ion chromatography (IC) for the analysis of Cl<sup>-</sup> and SO<sup>2-</sup><sub>4</sub>. Study 2 includes a thorough evaluation of the measured concentrations using the new workflow. Both a comparison with data from the operator, an inter-instrument test and an inter-laboratory test all show good agreement with the results achieved using the new technique. This not only validates the new technique; it also validates the historical data, upon which Study 1 is based.

Unique for this PhD project is the samples; these have been sent directly to DHRTC from the sampling points at the oil fields. Through contact with the field operator, we actively took part in the development of the sampling protocol. Thus, the samples are collected with eye to the purpose of the specific work presented in this thesis.

The analysis of these new samples, presented in Study 2, shows that the Ba<sup>2+</sup> concentrations in the PW samples are mostly below the lower limit of detection (LOD) of the previously used analytical method (IC). These levels have been detected using ICP-OES; for the majority of the samples the Ba<sup>2+</sup> concentration is in the range of 0.0 to 1.3 mg/L. A study on the scale potential of PW containing the low levels of both Ba<sup>2+</sup> and low levels of SO<sup>2-</sup><sub>4</sub> shows that scale formation is a risk even at these low concentrations since saturation conditions are met. This underlines the importance of a sensitive Ba<sup>2+</sup> analysis as that provided using ICP-OES.

Study 2, part 2 (Appendix A.3) covers an evaluation of the changes in the concentrations of the previously mentioned ions (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) over a period of one year, where the samples have been left for storage. In this time, nothing has been done to the samples; they were stored well-sealed, refrigerated (5°C) in the dark. In the study, no significant changes in the sample compositions were observed, except for  $Ca^{2+}$  (20% loss after one year), which most likely is lost due to precipitation of CaCO<sub>3</sub>. This is a valuable outcome and indicates that the produced water samples are still representative despite their "age" with respect to the major ions for when they were sampled. Often samples are stored in case of need for later analysis; eg. using improved methods, or analysis with different goals in mind; new questions caused by new knowledge etc. The samples included in this study are samples, which were collected using the sampling protocol developed at DHRTC and sent directly to DHRTC. These were all nonpreserved (that is; no acid added after sampling). PW samples are most often acidified to preserve Fe(II) and to minimize bacterial activity. The latter acts as a sink for  $SO_4^{2-}$ . In the presented study, no significant changes in the  $SO_4^{2-}$  concentrations are observed, suggesting that preservation may not be needed. The reason for the request of no preservation was that most often HCl is used. If the addition of HCl is not fully controlled and

documented, it will affect the accuracy of the determination of CI-.

An addition to the classification of end-members, suggested in the present thesis, is the concentrations of heavy metals in the produced water. A preliminary study, presented in Study 3, see Chapter 7, shows that the levels of five different heavy metals differ significantly between the fields included in the study. The included heavy metals cover  $Mn^{2+}$ ,  $Pb^{2+}$ ,  $Hg^{2+}$ ,  $Zn^{2+}$  and  $As^{2+}$ . Samples from the Halfdan, Kraka and Valdemar fields were included as the PWC from these fields differs significantly based on the classified end-members presented in Study 1. A clear distinction based on the heavy metals between the fields was found in the presented work.  $Pb^{2+}$  and  $Zn^{2+}$  were mainly measured at a significant level in water produced at the Valdemar field. Significant levels of  $As^{2+}$  is localized to the Halfdan field and  $Mn^{2+}$  to the Kraka field. This suggests the heavy metals are somewhat connected to the end-members. Water produced from the Kraka field is saline water, whereas produced water from the Valdemar field is classified by low salinity and high  $Ba^{2+}$  concentrations.

In the Danish North Sea, dispersed oil in produced water is the current target of detailed monitoring and cleaning procedures, as there are legal annual and absolute limits in effect for the amount of dispersed oil emitted to sea. The findings presented in Study 3 suggest that the levels of heavy metals emitted to the marine environment from production water could be a topic of further interest. The potentially problematic effects on the marine environment will depend on absolute concentrations in the discharged water, as well as the dispersion rates in the ocean. Accurate determination of the heavy metals in the produced water is a prerequisite for further studies.

The last work included in this thesis is a qualitative study of the dissolved organic species identified in nine produced water samples from the Halfdan field, which are a subset of the samples studied in Study 2. 15 distinct organic compounds are observed in all nine samples, and these include alcohols and saturated and aromatics acids. Compounds not observed in all nine samples are not discussed here, as this would require further detailed analysis, but could yield some interesting geographical differences. Some of the identified acids including octanoic acid, heptanoic acid and 3-methylbutanoic acid are common fatty acids found in crude oil and their degradation pathways in the marine environment could be important for a full evaluation of the consequences of emitting produced water from the oil production to the sea.

In summary, the work presented in this thesis has focused on an unique sample set of produced water acquired directly from individual oil producing wells by the operator in the Danish North Sea. The presented study has focused on the accurate determination of the concentrations of the major ions in the produced water, using state of the art analytical methods and novel workflows. The presented data is discussed both from a geochemical and a production chemistry perspective. The application potential is substantial as great challenges including scale mitigation, injection strategies and produced water.

# **10** Contributions

Besides the studies reported in this thesis, the author have contributed to the following during her PhD.

- Core flooding effluents were analysed using a similar workflow as that presented in Study 2. The core flooding experiments mainly focused on exploring different enhanced oil production strategies. Especially, the sensitive analysis of Ba<sup>2+</sup> was found useful.
- Fluids from an experiment studying the cation exchange between Mg<sup>2+</sup>-Ca<sup>2+</sup> were analysed using a similar workflow as that presented in Study 2. Also, the author supported in the process of designing and setting-up the exchange experiment. The sensitive of the ICP-OES proves itself useful as only small changes in the concentrations of both Ca<sup>2+</sup> and Mg<sup>2+</sup> were observed.
- Corrosion study fluids were analysed using a similar workflow as that presented in Study 2. Again, the sensitive analysis of Ba<sup>2+</sup> was found useful.
- The classified end-members (Study 1) have been used as input for a wide range of studies as part of the Radical Innovation Sprint initiated by DHRTC. These studies are titled:
  - Optiprobe: In situ pH and DO probes (2017)
  - Treatment of produced water recovery of salts and fresh water (2017)
  - Investigation of microbial souring mechanisms and testing natural antibiotics for prevention of microbiologically influenced corrosion (MIC) (2018)
  - Hydrocarbons in produced water: A misplaced resource for the bioproduction of the industrial commodity ectoine (2018)
  - Development of graphene filter for water treatment (2018)
  - Membrane emulsification can a stable and engineered emulsion enhance oil recovery? (2018)
  - DeZulf biological removal of sulphate from seawater (2019)
  - IPCC innovative process to combat corrosion (2019)
  - Microbial respiration of petroleum in fuel cells for electricity production (2019)
  - Tailored nano- and microemulsions to remove dispersed oil from produced water - can emulsions break emulsions? (2019/2020)
  - A novel sponge filter for simultaneous removal of oil and chemical additives from produced water (2019/2020)
  - The seafloor as a natural biofilter for cleaning produced water (2019/2020)

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# A Publications and manuscripts

## A.1 Paper 1

## Classification of and changes within formation water types in Danish North Sea Chalk: A study of the Halfdan, Dan, Kraka and Valdemar oil reservoirs

Contributions: Sofie N. Bergfors conceptualized the study together with Niels. H. Schovsbo, who suggested PCA as the analytical approach. Sofie N. Bergfors have collected and analysed all the data with support from Niels H. Schovsbo. Pictures were prepared as a collaboration between Niels H. Schovsbo and Sofie N. Bergfors. Niels H. Schovsbo wrote the section "2. Geological setting", the remaining manuscript is written by Sofie N. Bergfors. Niels H. Schovsbo and Karen L. Feilberg both functioned as supervisors. All authors performed scientific and grammatical revisions of the final manuscript.

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## Classification of and changes within formation water types in Danish North Sea Chalk: A study of the Halfdan, Dan, Kraka and Valdemar oil reservoirs

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#### ABSTRACT

The ionic composition of produced water from four oil producing chalk fields in the Danish North Sea has been interpreted to shed light on the temporal and regional variations in the water composition. The data includes 8749 samples, covering 157 wells, analyzed for eight ions. The data dates back to the start of production (1972–2007) and the most recent data is from 2015. The variations are viewed in a regional context with respect to subsurface geology, fluid migration and production strategy since parts of the fields have been extensively water flooded by injection of seawater. We present results from both time series analysis and from multivariate statistical methods and show that produced water across the four fields, up to 55 km apart, show gradual changes in the composition reflecting regional scale hydrodynamics as well as subsurface geology. We use multivariate statistical analysis to extract end-member compositions to facilitate comparison between basins and for an evaluation of scale and corrosion risk. The data analysis shows five main water types. These are mainly differentiated by salinity and the concentrations of the divalent cations. The study is discussed in the context of examination of interconnection between close-lying fields including aquifer support and distribution of principal ions associated with corrosion and scale formation.

#### 1. Introduction

Produced water from oil production wells is routinely analyzed for its ionic composition, in order to monitor the well performance and track potential scale precipitation and corrosion in the wells (Jones et al., 2006; Vazquez et al., 2015). Certain detrimental scales in the wells and installations are an operational risk and very costly to remove, and the potential precipitation of these is dependent on the concentrations of trace ions in the flowing water. Consequently, an interest in monitoring the chemical composition of the produced water reliably has been existing from the very early stage of production. This applies especially in the North Sea Chalk, which is composed of clay sized carbonate grains that are potentially chemically and physically reactive during production (McCartney et al., 2005; Austad et al., 2008; Puntervold and Austad, 2008; Puntervold et al., 2009). In recent years, the interest in produced water chemistry has increased globally. In a paper from 2011, Schlumberger states that "water properties contain a wealth of information that can be used to significantly impact field economics" (Abdou et al., 2011). The water composition informs the choice of enhanced oil recovery (EOR) techniques, production management materials, water handling strategy and scale inhibition (Houston et al., 2006).

The chemical composition of produced water reflects both *in-situ* formation water and injected water, which is typically modified seawater (removal of  $O_2$ , filtration, production chemicals). None of these have constant properties, neither with respect to subsurface 3D hydrodynamics nor with respect to production time and design. Thus, the composition of produced water is known to vary between different fields but also within the same field, which reflects the complex interplay of processes (Vazquez et al., 2015; Schovsbo et al., 2016; Schovsbo et al., 2017; Schovsbo et al., 2018; McMahon et al., 2018). Despite this, relatively little work has been done to map these differences. The reported research have mainly focused on the mapping of the Cl<sup>-</sup> concentration as this ion is considered a relatively inert ion, which is

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measurably diluted upon seawater injection, as the formation water is typically characterized by significantly higher total salinity (McCartney et al., 2005; Houston et al., 2006; Vazquez et al., 2015). Therefore, it is the simplest tracer for the changing proportion of injected seawater relative to formation water. As a consequence, Cl<sup>-</sup> is used to study flow patterns and predicting the mixing front in reservoirs (McCartney et al., 2005; Houston et al., 2006; Vazquez et al., 2015). This simple approach is advantageous when high salinity contrast exists between formation water and injected water. Also, increased SO<sub>4</sub><sup>2-</sup> concentrations are routinely used as a marker for breakthrough of injection water (Shaw et al., 2010, 2012; Jimoh et al., 2017). However, the more ions that are included in a produced water chemistry (PWC) study, the more information is to be extracted. This applies to less saline reservoirs and, particularly, in potentially reactive carbonate reservoirs. For example, the variation of K<sup>+</sup> concentration can be used as an indicator for clean-up efficiency of well contaminated by completion fluids in wells where a potassium based mud system is used (Caenn et al., 2011). In addition, monitoring of potential determining ions such as Ca<sup>2+</sup> and Mg<sup>2+</sup> during water injection may convey important information about recovery mechanisms as these can be indicators of dissolution and adsorption on the surface of the rock (McCartney et al., 2005; Puntervold and Austad, 2008; Puntervold et al., 2009). The original water present in the subsurface prior to any injection is the formation water which is generally characterized by high salinity compared to seawater and by the (relatively high) content of trace ions such as  $Ba^{2+}$  and  $Sr^{2+}$ . Seawater is the standard injection water in many water flooded reservoirs in the study area. It has a total salinity of about 35 g/L and is characterized by a SO<sub>4</sub><sup>2-</sup> content of 2700 mg/L. It is common practice in many fields to treat the seawater prior to injection (additional to O2 removal and filtration) to limit the risk of accumulation of sulphate scales (Hardy and Simm, 1996). Due to the different compositions of formation water and seawater, the monitoring of the ionic composition of the produced water gives an indication of the extent of mixing of seawater and formation water in the subsurface. This combined with temperature measurements, the mixing of formation water and injection water, is used to monitor the extent of seawater breakthrough in wells. This study includes compositional data with eight ions: Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>,  $Ca^{2+}$ ,  $Ba^{2+}$ ,  $Sr^{2+}$ ,  $Cl^-$  and  $SO_4^{2-}$ . The detailed data has been made available and is studied within and across four chalk fields in the Danish North Sea: The Halfdan, Dan, Kraka and Valdemar fields. The Halfdan and Dan fields are currently water flooded, and the Kraka and Valdemar fields are potential candidates for water flooding in the future. Previously, N. H. Schovsbo et al. have published two studies with similar objectives as this study (Schovsbo et al., 2016, 2017). From a minor data set (33 water samples), four water types are classified across the entire Danish North Sea (Schovsbo et al., 2016). These water types are very similar to those presented later in this study, though discussed to a much smaller degree. The present study substantially expands on the previous work as it is based on 250 times more individual samples. These identified water types were further studied in a later publication by N. H. Schovsbo et al., in which a discussion of temporal changes in the Halfdan field is touched upon (Schovsbo et al., 2017). This discussion includes 390 water samples distributed over 9-11.5 years. They find that the introduction of sulphate with the injection water is the cause for the major changes regional. The study presented here included significantly more samples (8000+) distributed over the entire lifetime of the wells; and additionally, this work pays more attention to the underlying geochemical processes governing the composition of the produced water and the changes therein.

We apply multivariate statistical methods as a classification tool of the produced water; and thermodynamic modelling (Extended UNI-QUAC) to investigate the thermodynamics of the water and potential scale formation. Together this will provide input to production strategies, scale prevention and mitigation strategies of both mature and new fields. Also, the observed trends in the PWC contributes to classification of formation water in order to establish the evolution and original formation of the reservoirs, which will lead to an even better understanding of fluid migration patterns in the North Sea area.

#### 2. Geological setting

The oil province in the Danish North Sea is part of the prolific Central Graben petroleum system (Fig. 2). The Graben formed as a result of rifting in the Jurassic and, subsequently, subsidence that resulted in deposition of km thick Jurassic source rock (Petersen and Hertle, 2018). The primary source of gas in the fluvial to lacustrine Middle Jurassic coaly source rock and the primary source of oil is the marine Upper Jurassic Farsund Formation (Petersen et al., 2013). The vast majority of the oil and gas resource is trapped in Cretaceous-Paleogene chalk which is composed of the remains of calcareous microorganism shells (Fig. 1) (Megson, 1992; Hjuler and Fabricius, 2009). The main kitchen areas for oil generation were in the Tail-End Graben and in the northern part of the Salt Dome Province (Fig. 2) (Ponsaing et al., 2020). Subsidence led to deep burial and maturation of the gas bearing Jurassic sequence already in the Cretaceous (Petersen and Hertle, 2018). The main phase of oil expulsion occurred in the Paleocene-Eocene and it is generally assumed that the main filling of the fields took place as long distance



Fig. 1. Stratigraphic overview of the Danish North Sea with indications of main reservoir ages for the Chalk fields discussed.



Fig. 2. Map of oil and gas field locations in the Danish North Sea.

migration of oil from North to the South (Albrechtsen et al., 2001; Vejbæk et al., 2005; Petersen and Hertle, 2018). Evidence for hydrodynamic movement of the fluids has only been made indirectly from distribution of pressure (Megson, 1992; Japsen, 1998; Vejbæk et al., 2005). On a regional scale the pore pressure in the chalk is strongly overpressured with a profound center of over pressure in the southern part of the Norwegian part of the Central Graben. From here the level of pressure decrease towards the Graben rims. Within the Danish Central Graben this pressure decrease amounts to 8 psi/km (55 kPa/km) in a North to South direction, which has been translated into a water flow velocity within the chalk to 2 km/Ma (Vejbæk et al., 2005).

#### 2.1. Overview of fields

Data from four producing chalk fields has been analyzed (Figs. 1 and 2). The reservoir age ranges from the Lower Cretaceous, through the Tor Formation and to the Paleogene Ekofisk Formation. Overall, the reservoirs are very similar; they all consist of chalk, are very porous (25–45%), and have low matrix permeability (0.1–3 mD). The reservoir quality varies with stratigraphy with the least permeable reservoir being the Tuxen Formation (Jakobsen et al., 2004). Below, a short synopsis of the fields are presented. Detailed maps of the four fields are given in the Supplementary Material Figs. 1–4.

#### 2.1.1. The Halfdan field

The Halfdan field was discovered in 1999 and production was started within that same year (Albrechtsen et al., 2001). The field is estimated to hold about 1500 MMB oil in place (Rasmussen et al., 2005). The field has in total 38 oil producing wells and 27 water injection wells applying seawater as the injection fluid. Additionally, the field has 16 gas producing wells (Halfdan North East (Sif/Igor area), see Fig. 2) (Danish Energy Agency, 2013). The field is developed in an alternating pattern of km-long multistage horizontal producer and water injector wells aimed at maximum water sweep efficiency by applying the Fracture Aligned Sweep Technology (FAST) concept, developed by Mærsk Oil (Lafond et al., 2010). The production is primarily from the Upper Cretaceous Tor Formation made up by almost pure unfractured chalk similar to that found at the Dan field. Porosities are around 25-35% and permeabilities 0.5-2.0 mD (Rasmussen et al., 2005). The oil is trapped in a hydrodynamic quasi-equilibrium owing to the low permeabilities of the chalk and the oil is currently on a migration route towards the south into the Dan field structure and the boundary to the North flank of the Dan field

is somewhat arbitrary (Albrechtsen et al., 2001). The present day configuration of the Halfdan field is that of syncline located between the Dan and Skjold fields (Fig. 2) (Rasmussen et al., 2005). Salt in the subsurface of the Halfdan field is present to the North West in the Skjold structure and to the south in the Dan Central Dome (Jacobsen et al., 1999; Albrechtsen et al., 2001; Danish Energy Agency, 2013). A detailed outline of the Halfdan field and definitions of structural elements are described by Calvert et al. (2016). It is noted, that gas is also produced from the Halfdan field (Supplementary Material Fig. 1).

#### 2.1.2. The Dan field

The Dan field is located in the southern part of the Salt Dome Province just south of the Halfdan field (Fig. 2) and is the longest producing field of the four presented in this study. The field was discovered in 1971 and has been producing since 1972. From 1989, the reservoir has been extensively water flooded by injection of seawater to maintain pressure. The Dan field has 61 oil producing wells and 48 gas producing wells (Danish Energy Agency, 2013). Geologically, the field is divided by a main fault into two main blocks. These are intersected by a number of smaller faults. The reservoirs are the Upper Cretaceous Tor Formation similar as to the Halfdan field and the Paleogene Ekofisk Formation. The oil is trapped in a four-way closure formed by salt movements. The northwestern flank of the field show a continuous oil column to the Halfdan field and the accumulation here is developed jointly from both Dan and Halfdan platforms (Jacobsen et al., 1999; Albrechtsen et al., 2001).

#### 2.1.3. The Kraka field

The Kraka field is located in the southernmost part of the Salt Dome Province and was discovered in 1966 (Figs. 2 and 1). The field is estimated to have an original oil in place of 200 MMB. Despite the early discovery, it was not put in production until 1991. It has eight producing wells, all producing from a natural pressure gradient and, therefore, no water injection is applied. The reservoir rock is composed of fractured Paleogene Ekofisk Formation and the oil is trapped in a four-way closure formed by salt movements (Thomasen and Jacobsen, 1994). The reservoir is characterized by high water saturation, has a medium-good porosity around 30%) and low matrix permeability (1–3 mD). Effective permeabilities due to fracturing is about 8 mD (Rasmussen et al., 2005; Danish Energy Agency, 2013).

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#### 2.1.4. The Valdemar field

The Valdemar field is located in the northern most part of the Salt Dome Province, just south of the Tail-End Graben (Fig. 2). The field is divided into two sections: North Jens and Bo (Supplementary Material Fig. 3). North Jens was discovered in 1985 and has been producing since 1993. Bo was discovered in 1977 and has been on stream since 2007. In total, the Valdemar field has 21 oil producing wells and two gas producing wells. The oil is trapped in an inversion tectonic structure. (Jacobsen et al., 1999; Jakobsen et al., 2004), and is produced by natural drainage and, thus, no water injection is made (Danish Energy Agency, 2013). The reservoir is composed both of pure Upper Cretaceous Chalk and of Lower Cretaceous Tuxen and Sola formations with a relatively high clay content. The Lower and Upper Cretaceous chalk reservoirs are non-interacting and the primary production is from the chalk in the Lower Cretaceous Tuxen Formation. The Valdemar field represents the lowest permeable chalk comparable to other North Sea reservoir units.

#### 2.2. Field connectivity

The petrophysical properties of the North Sea chalk reservoirs are greatly governed by a high porosity and a low permeability (Megson, 1992; Albrechtsen et al., 2001; Vejbæk et al., 2005). As a consequence, a geological time scale is needed to equilibrate the system and the fluids within. No structural closure has ever been reported in the Halfdan field and the gas-oil and water-oil contacts are found to exhibit an apparent tilt from east to west (Albrechtsen et al., 2001). According to Albrechtsen et al., this tilt reflects hydrodynamic forces driving water and oil towards Southwest. Furthermore, from modelling the fluids, they have found that the Halfdan field exhibits an active migration of oil from Northwest into the Dan field. Vejbæk et al. have estimated the pressure gradient in the water zone in the Kraka field and translate it into a flow rate of approximately 0.9 km/Ma to the southeast on the assumption, that this flow is only in the matrix. Also, they highlight that the Dan-Halfdan field system is fully dynamic and both water and oil flow within this system with a flow rate of 2 km/Ma (Vejbæk et al., 2005).

#### 3. Methods

#### 3.1. Data

Data from produced water analysis of four fields (Halfdan, Dan, Kraka and Valdemar) have been included in this study. In total, the data covers 157 wells distributed as follows: 40 wells on the Halfdan field (3668 samples), 88 wells on the Dan field (4895 samples), seven wells on the Kraka field (71 samples), and 26 wells on the Valdemar field (140 samples), which in total gives 8749 analyses. The data covers analyses of the ionic composition of produced water from the very early stage of production (Dan: 1972; Halfdan: 1999; Kraka: 1991; Valdemar, North Jens: 1993, Bo: 2007) and up to and including 2015. For the majority of the analyses the sampling date together with all concentration measurements of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Cl<sup>-</sup>, and SO<sup>2-</sup> - and for a few samples also Br<sup>-</sup> - are available. The analyses have primarily been carried out by ion chromatography, and some early analyses include titration. The water samples have been gathered off-shore at quarterly intervals on average and transported on-shore for analysis in the operator's laboratories. The primary goals of the sampling have been monitoring of the breakthrough of injection water (total salinity, Cland SO<sub>4</sub><sup>2-</sup>), corrosion and scale potential (Ba<sup>2+</sup> and Sr<sup>2+</sup>) and inhibitor performance. Immediately after sampling, acid has been added to the produced water (HCl and/or HNO<sub>3</sub>), in order to prevent bacterial activity and limit the risk of solid precipitation in the samples. No further treatment of the samples prior to the time of analyses has been recorded. The samples are filtered using a 0.2  $\mu$ m filter, followed by analysis of cations and anions by ion chromatography, according to the protocol used by the oil field operator.

The data, this study is based upon, is provided to us from our partner,

Total, in the aim of promoting research within the oil and gas industry. Previously, the PWC data presented in this work was confidential but is now made available with only the specific well names anonymized.

#### 3.2. Data cleaning and preparation

For a few of the samples, the reported composition does not include values for all eight ions (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Cl<sup>-</sup>, and  $SO_4^{2-}$ ). For 1228 samples, corresponding to 14% of the total number of data points, the Na<sup>+</sup> concentration was not reported. And for less than 5% of the samples one of the remaining concentrations was either missing or the data provided appeared to have unrealistic high or low values (eg.  $[SO_4^{2-}] = 3 \text{ mg/L}, [Cl^{-}] = 40 \text{ mg/L} \text{ and } [Cl^{-}] = 196000 \text{ mg/L}$ L). We have considered three approaches to mitigate these discrepancies and prepare the data for analysis: a) Include all data, b) estimate the concentration of odd data points from the charge balance, or c) disregard the entire sample sequence as erroneous. Option b was used for all concentrations of Na<sup>+</sup> presented in this study (these are denoted Na<sup>\*</sup>). A neutral solution was assumed and the Na\* was estimated using the concentrations of the remaining ions. For the 86% of the data the ratio between estimated Na<sup>+,\*</sup> estimated and Na<sup>+</sup> reported was 1.00 (Supplementary Material Fig. 5), suggesting that unaccounted substances such as bicarbonate and organic acid do not significantly impact the predictability of Na<sup>+</sup> from the ion charge. We therefore used the estimated Na<sup>+,\*</sup> for the whole data set. For unrealistic high or low concentrations option c was applied. The following thresholds have been used:  $Ca^{2+} > 10000$  mg/L was removed, K<sup>+</sup>> 1200 mg/L was removed, full data set with Na<sup>+,\*</sup> estimated to be < 0 mg/L. The removed data is included in the presented cross-plots. Based on this filtering the data set was reduced from 8749 samples to 8579 samples.

To allow for data pre-processing, samples reported with a value zero was treated as "rounded zero" according to Martin-Fernandez et al. and replaced with a value that represents the lower level of detection (Aitchison, 1986; Martin-Fernandez et al., 2003). This was only applicable for  $\mathrm{Sr}^{2+}$  and  $\mathrm{Ba}^{2+}$  where 5 mg/L and 1 mg/L was used, respectively. This method is only recommended when the subset with incomplete data amounts no more than 10%. In our data set, 1% of the samples are lacking information on the  $\mathrm{Sr}^{2+}$  concentration. For  $\mathrm{Ba}^{2+}$  this percentage is 80. Thus, it introduces a significant disorder to the general structure and we, therefore, only include  $\mathrm{Ba}^{2+}$  in the overview of the data (Figs. 3, 4 and 9) and leave it out in the detailed studies (Figs. 7 and 8).

All data analyses in this work are based on centered logratio (clr) transformed data. This transformation is often applied to geochemical data and is considered as the generally accepted standard, particularly for compositional data (Aitchison and Greenacre, 2002; Buccianti and Pawlowsky-Glahn, 2005; Valls, 2008; Filzmoser et al., 2009a; Filzmoser et al., 2009b; Aitchison, 2015). When Ba<sup>2+</sup> is excluded from the data set, a new clr transformation must be performed on the remaining data prior to the principal component analysis (PCA).

#### 3.3. Principal component analysis

Principal component analysis, PCA, is a multivariate data analysis method often used to reveal hidden data structure; trends and outliers (Esbensen and Swarbrick, 2018). By the use of orthogonal transformation, it converts a set of observations of possibly correlated variables (in this case ion concentrations) into a set of linearly uncorrelated variables. These are called the principal components (PC). The first principal component (PC-1) lies along the direction of the maximum longitudinal variance in the data set. The second PC (PC-2) lies along the direction of the second largest variance orthogonal to PC-1. PC-3 lies along the third largest variance, orthogonal to both PC-1 and PC-2, and so forth (Esbensen, 2002).

The PCA is performed with The Unscrambler X 10.5.1 software package (Esbensen, 2002; Esbensen and Swarbrick, 2018). Because the

outliers are removed from the data set, classical PCA with clr transformed data is sufficient. Otherwise, robust PCA with isometric logratio (ilr) transformed data would have been the method of choice (Filzmoser et al., 2009; Nordhausen et al., 2015). Seawater composition, defined by Schovsbo et al., is included in the PCA model to precisely identify its position compared to the analysis (Schovsbo et al., 2016). The inclusion of the seawater composition does not impact the outcome of the model.

#### 3.4. Thermodynamic modelling

Extended UNIQUAC is a thermodynamic model designed for electrolyte solutions. The model can be used to predict thermodynamic properties and phase equilibria of liquid-liquid, solid-liquid and gasliquid systems and is described in detail by K. Thomsen (2005). Here, it is applied to calculations of the potential for carbonate and sulphate scaling. It provides general phase equilibrium calculations for aqueous solutions with the ions Na<sup>+</sup>, H<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup>, Cl<sup>-</sup>, OH<sup>-</sup>,  $SO_4^{2-}$ ,  $HSO_4^{-}$ ,  $CO_3^{-}$ ,  $HCO_3^{-}$  under the given pressure and temperature conditions. K<sup>+</sup> is included as Na<sup>+</sup>. The model provides the saturation index (ionic activity product divided by the solubility product) of the solids that can potentially precipitate from the solution. In the cases where the saturation index is higher than one and the precipitation of solids thermodynamically is possible, there is the potential risk of scale formation. Many factors affect the actual scaling potential, including kinetics, flow patterns in the wells, sticking factor for a given solid to the surface and the nature of the surface of the well tubing, but the first prerequisite is a state of supersaturation. As the concentrations of key ions vary significantly from well to well, the risks of formation of hard to remove scales needs to be evaluated on a case to case basis. The data provided in this study is used in the model to give an indication of the variability of scaling risk across these fields.

During the transfer from the sampling point at the well to the laboratory, a sample may meet distinctively different (physical) environments: Reservoir conditions, ambient conditions and cool storage conditions. The latter because most samples have been stored in at 5  $^\circ \text{C}$ prior to analysis. Every change in conditions may cause a risk of precipitation. In the data, the HCO<sub>3</sub> concentration is not included, which is required to account for as the system is expected to be saturated with respect to calcite (as it is a chalk reservoir) (Rasmussen et al., 1992). Jones et al. have measured the HCO3 concentration in a selection of formation waters. They found that the HCO<sub>3</sub><sup>-</sup> concentration is approximately 400 mg/L for the Dan and Halfdan fields (Jones et al., 2006). Hence, this value is used for reservoir conditions. (Also, we use the reservoir pressure reported here (Jones et al., 2006).) The ambient level of HCO3 varies with seasons and locations. Often, slight variations within days are also observed (Ray and Engelhardt, 1992; Salt et al., 2013). From literature, the average concentration of  $HCO_3^-$  in seawater is approximately 140 mg/L (Dickson, 2001). Below is given the assumed pressure, temperature and  $\mathrm{HCO}_3^-$  concentration at the three different conditions used in the Extended UNIQUAC model. For Valdemar, which is a deeper Tuxen reservoir, two sets reservoir conditions are included. One which has higher pressure and temperature (Copestake et al., 2003).

- Reservoir conditions [from (Jones et al., 2006)]: 17 000 kPa, 70 °C, 400 mg/L HCO<sub>3</sub>.
  Valdemar [from (Copestake et al., 2003)]:37 000 kPa, 86 °C, 400 mg/L HCO<sub>3</sub>.
- Ambient conditions: 100 kPa, 20 °C, 140 mg/L HCO<sub>3</sub><sup>-</sup>.
  Cool storage conditions:
- 100 kPa, 5 °C, 140 mg/L HCO<sub>3</sub>.

It is noted that the added acid has not been included in the Extended UNIQUAC model. This is relevant for the ambient conditions and cool storage conditions. Also, it is highlighted that the model will always predict precipitation once the SI is above one, but in reality the solution may be supersaturated (with SI > 1) without solid being formed. The addition of acid to the samples promote the supersaturation without precipitation.

#### 4. Results

#### 4.1. Temporal changes

Fig. 3A shows the changes in the ionic composition of produced water from a representative Halfdan well. The Na<sup>+</sup> and Cl<sup>-</sup> concentrations decreases slowly from 35 000 mg/L  $\rm Cl^-$  and 20 000 mg/L  $\rm Na^+$  in the first 2500 days (7 years) of production to a stable plateau of 27 000 mg/L Cl<sup>-</sup> and 16 000 mg/L Na<sup>+</sup>. The SO<sub>4</sub><sup>2-</sup> concentration shows an inverse correlation to the Cl<sup>-</sup> and Na<sup>+</sup> concentrations. The level increases from approximately 200 mg/L at start of production to a stable plateau of 1300 mg/L after 2500 days, and at the same point in time the Na<sup>+</sup> and Cl<sup>-</sup> have reached a stable plateau. The trend reflects the water cut in the production, which is less than 2% in the first 1500 days of production (4 years). This suggests the water produced during this period is formation water. The water composition shifts after 2500 days (the time of injection water breakthrough) to a composition, which more closely resembles seawater (see Table 1 for this composition). At this point in time, the water cut increases significantly. However, the ionic composition of the produced water does not exactly match the injected seawater since the produced water is slightly higher in Cl<sup>-</sup> and lower in  $SO_4^{2-}$ . This suggests a contribution from formation water in the production also after injection water breakthrough has occurred.

Ca<sup>2+</sup> levels above 1000 mg/L are observed within the first 1000 days of production. These levels most likely reflect the level in formation water. Later in the production period,  $\mathrm{Ca}^{2+}$  decreases as the PWC is changing from the formation water signature to a mixed water (formation water and seawater) signature. This is mirrored by the increase in Mg<sup>2+</sup> from about 300 mg/L in formation water to 700 mg/L during later production (Fig. 3B). This shift in the  $Ca^{2+}/Mg^{2+}$  ratio can be due to the mixing of seawater and formation water with potentially some contribution from cation exchange, which can take place on the chalk surfaces inside the reservoir. Supplementary Material Fig. 6 shows the correlation between  $Ca^{2+}/Mg^{2+}$  and  $SO_4^{2-}$ , and the correlation between the concentrations of  $Mg^{2+}$  and  $SO_4^{2-}$  for the three wells included in Fig. 3. Supplementary Material Fig. 6 shows that the Mg<sup>2+</sup> concentration increases linearly with the  $SO_4^{2-}$  concentration, indicating that the increase in the  $Mg^{2+}$  concentration is caused by the introduction of injected (sea)water. The trend observed for the  $Ca^{2+}/Mg^{2+}$  vs.  $SO_4^{2-}$  plot up to a SO<sub>4</sub><sup>2-</sup> concentration of 1000 mg/L does not have a straightforward explanation. It may be caused by extremely high  $Ca^{2+}$  concentrations in the initially produced water. Cation exchange between Ca<sup>2+</sup> and  $Mg^{2+}$  is a typical mechanism proposed for enhanced oil recovery (EOR), but evidence for this is not clearly observed here (Rasmussen et al., 1992; McCartney et al., 2005; Austad et al., 2008; Puntervold and Austad, 2008; Puntervold et al., 2009).

The Dan field represents a much more intensively water flooded reservoir than the Halfdan field since this process has been in use in some parts of the field since 1989 (Danish Energy Agency, 2013). In Fig. 3C, the chemical evolution through 8000 days (22 years) is shown for a representative Dan well. The profile is quite similar to the Halfdan well and shows that Na<sup>+</sup> and Cl<sup>-</sup> stabilizes after 2100 days (6 years) at concentrations similar to those observed at the Halfdan field. Fig. 3D shows that SO<sub>4</sub><sup>2-</sup> reaches a plateau at about the same time as Na<sup>+</sup> and Cl<sup>-</sup>, i.e. at about 2000 days. This may be caused by breakthrough of the injected water. Furthermore, the same trends as for the Halfdan field are observed in the concentrations of Ca<sup>2+</sup> and Mg<sup>2+</sup>; they are inversely correlated and stabilizes at the same time as Na<sup>+</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>.

Fig. 3E and 3F shows the evolution of the PWC in samples from one Valdemar well. The Valdemar field has not been water flooded and is producing solely from natural pressure depletion. Analysis of the time



**Fig. 3.** Temporal changes in the water composition of produced water from Well A: Halfdan, Well B: Dan, and Well C: the Valdemar field. For the wells, plot A, C and E show the change in the concentrations of Na<sup>+</sup> and Cl<sup>-</sup> and plot B, D and F show the evaluation of K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>. The blue curve shows the water cut (vol. % water) of the produced liquid (right axis). The water cut for the Valdemar field has not been provided. Arrows mark events that could affect the compositions.

series is mostly aimed at monitoring possible trends within the aquifer and to update potential scale models for predicting precipitating minerals. Therefore, the available data on the Valdemar field is sparse compared to that from the Halfdan and Dan fields. Here, it is found that all ions have reached a relatively stable plateau at the time of the second sample, which is sampled after 1000 days (3 years) of production. Two aspects of the chemical composition is markedly different from both the Dan and Halfdan wells: 1) The Cl<sup>-</sup> concentration is significantly lower (22 000 mg/L at start to 17000 mg/L when stable) indicating a salinity lower than present day seawater, and 2) the Ba<sup>2+</sup> concentrations are found to be higher than on the Dan and Halfdan fields and significantly higher than the analytical lower detection limit.

The Lower Cretaceous chalk in the Valdemar field has, by far, the

lowest permeability of all chalk types in the North Sea. This combined with the absence of injected seawater makes the chemical impact from well workovers on the data especially evident. The effect from this on the K<sup>+</sup> is, thus, significant with a spike in the concentration at the time of the workover. Also, high initial  $SO_4^{2-}$  concentrations (up to 900 mg/L) that continuously decline (to 0–100 mg/L) are evident of the lack of seawater injection.

Because very limited data from the Kraka field is available to us, we chose not to present the data here.

Fig. 3 illustrates only a minor fraction of the total data available to us. In order to examine and illustrate the impact of production time on the PWC, a PCA of the total 8579 samples from the four fields (Fig. 4 and Supplementary Material Fig. 6) have been prepared. In the PCA, all data Table 1

The composition of the localized end-members (EM). For each EM the average composition and the 10% percentile (P10) composition are given. "Mix X" is the composition of a mixture of 40% EMX (X = 1, 3, 4, 5) and 60% EM2.

End-member Typical occurrence		Na <sup>+</sup> mg/L	K <sup>+</sup> mg/L	Mg <sup>2+</sup> mg/L	Ca <sup>2+</sup> mg/L	Sr <sup>2+</sup> mg/L	Ba <sup>2+</sup> mg/L	Cl <sup>-</sup> mg/L	SO4 <sup>-</sup> mg/L
1 Halfdan N.	Mean P10 Mix 1	15931 20089 15228	154 246 371	210 304 987	891 1354 881	91 133 56	12 18 8	27003 33397 26191	42 77 1720
2 "Seawater"	Mean P10	10994 11987	379 455	1241 1442	480 565	5.0 5.1	1.0 1.1	20049 21387	2352 2816
3 Dan (and Halfdan S.)	Mean P10 Mix 3	26648 29973 19181	210 280 385	408 553 1086	2611 4219 2027	328 424 173	1.0 1.1 1.0	47023 52279 33744	560 672 1958
4 Valdemar	Mean P10 Mix 4	10211 12430 12164	122 186 347	100 139 921	371 586 573	65 102 44	45 71 29	16881 20684 21106	36 80 1722
5 Kraka	Mean P10 Mix 5	41546 43970 24780	210 246 371	514 597 1104	2671 3460 1723	363 437 178	1.0 1.3 1.0	70493 74467 42619	482 562 1914
Seawater (Schovsbo	et al., 2016)	10780	400	1280	410	20	0.0	19350	2710

points are grouped in three temporal bins. Group 1 represents samples from the first three years of production for a given well. Group 2 represents samples produced between three to ten years of production and, lastly, group 3 represents samples of water produced after ten years of production. For all wells, the zero point is the date of the first available analysis point typically measured within the initial well start-up, i.e. within the first months of production.

In Fig. 4, the three groups are indicated by the blue, grey and white data points. The first two components in the PCA model accounts for a total of 86% of the variance in the data set. On the loading plot (Fig. 4B), four main groupings of the clr normalized elements can be seen:  $Ca^{2+}$ ,  $Cl^-$  and  $Na^{+,*}$  plot at positive PC-1 and negative PC-2;  $Sr^{2+}$  plots at same signs but higher loading values;  $K^+$  and  $Mg^{2+}$  plot at negative PC-1 and positive PC-2;  $SO_4^{2-}$  with high negative PC-1 and negative PC-2 loadings.

The sample relationship is shown on the accompanying PCA score plot (Fig. 4A). In terms of water types, the samples that plot with high negative PC-2 score and positive PC-1 scores are highly saline with low  $SO_4^{2-}$ . This is typical for water found in fields atop salt domes such as the Kraka field. Samples that plot with high negative PC-1 values have low salinity with high  $SO_4^{2-}$  content and are compositionally similar to the

injected seawater. Lastly, samples plotting with high positive PC-2 values all have high  $Ba^{2+}$  concentrations and corresponding low  $SO_4^{2-}$  concentrations, similar to water from the Valdemar field.

In Fig. 4, it is observed that samples representing the first three years of production show a larger variance in K<sup>+</sup>, which suggests they are more affected by the completion fluids. The completion fluids contain, among other chemicals, KCl, which is used to stabilize the downhole mud system. All samples from the first ten years of production are equally spread across the PC-1 axis. However, for the wells that are subject to water injection the spread along the PC-1 axis decreases with time. Thus, the produced water becomes more and more similar over time. This is most likely due to the influence of water flooding; the injected water has roughly the same compositions for all the water flooded wells. The water produced after 10 years is only marginally impacted by the  $Na^+$ - $Cl^-$ - $Sr^{2+}$ (- $Ca^{2+}$ ) component. After this point in time,  $Mg^{2+}$ -SO<sub>4</sub><sup>2-</sup> is found to be the strongest component. Also,  $Ba^{2+}$  is found to be a significant component. This suggests that these are the components that are most affected by the production. The variance in  $Mg^{2+}$  may be caused by its exchange with  $Ca^{2+}$ . It is known that  $SO_4^{2-}$  is affected (increasing) by the introduction of seawater into the reservoir. And, oppositely,  $Ba^{2+}$  is depleted as a consequence of water injection



Fig. 4. Temporal changes in the water composition at all four fields. A) PCA score plot, B) PCA loading plot. The boxes represent the five localized end-members (EM1 - EM5).

since it is not present in the injected seawater. Again, we note that the  $Ba^{2+}$  concentrations carry a large uncertainty (Section 5.1).

#### 4.2. Validation of data

We have carried out a set of tests to ensure the quality of our data analysis. First, the pre-processing of the raw data, where samples containing unrealistic values, which are likely due to database entry errors, were excluded from the data set. Secondly, a robustness test towards the Na<sup>+,\*</sup> and Cl<sup>-</sup> concentrations has been carried out. A full PCA analysis, including the clr transformation, similar to the results presented has been carried out. The PCA plots show the exact same trends when Na<sup>+,\*</sup> and Cl<sup>-</sup> is excluded. This holds true for all combinations of principal components (Supplementary Material Fig. 11). This demonstrates that the Na<sup>+,\*</sup> and Cl<sup>-</sup> concentrations explain the least amount of variance in the data (compared to the other ions), thus outliers in the Na<sup>+,\*</sup> and Cl<sup>-</sup> series have little effect on the overall PCA. Because of this, the rough assumptions drawn to estimate Na<sup>+,\*</sup> (described in Section 3.2) are more acceptable. Third, the cross-plots (Section 4.4) help identify contaminated samples which behave as outliers when compared to the rest of the samples. Often these samples are characterized by unusually high concentrations of  $Ca^{2+}$  (>10000 mg/L) and K<sup>+</sup>(>1200mg/L). Finally, a PCA including all data, not clr transformed but only autoscaled by subtracting the mean and dividing by the standard deviation, has been carried out.

Compared to treatment and identification of outlier we find that substitutions for handling zeros pose the largest impact on data analysis and thus robustness of the results. We find that reliable data analysis can only be performed where zeros has been substituted for less than 10% of the data. We tested the value used of 0 substitution for  $\mathrm{Sr}^{2+}$  and  $\mathrm{Ba}^{2+}$  and it was found that substituting with unrealistic low values (0.1 ppm) or high values (10 ppm) compared to reported low values impacted the data analysis.

In some cases, several samples collected at the same day have been analyzed. Analysis of the mean and standard deviation of the daily variation is presented in Supplementary Material Table 2. This shows that the long-term variations exceed the daily variations (expressed as the standard deviation) significantly, thus allowing for conclusions on the long-term observed trends.

#### 4.3. Classification of water types

Based on the PCA model of all data (Fig. 4), five end-members have been identified. The end-members represent both naturally defined groupings in the PC-1 and PC-2 space (EM2, EM3, EM4) and field based end-members such as EM5 for the Kraka field and EM1 for the Halfdan field. EM2 represent a seawater-like type of water, which is a result of extensive water flooding. It is produced at Halfdan and Dan. EM3 represents water, most likely original formation water less affected by the injection of seawater, from Dan and Halfdan South, and EM4 water is characterized by low salinity and high  $\mathrm{Ba}^{2+}\!\!,$  as water produced from Valdemar. The end-member grouping have importance for both scale considerations (high ion strength as found in EM4 and EM5) or for understanding the regional fluid movements (eg. EM1). The end-member composition was calculated based on the 58-187 samples defined in Fig. 4 (shown with boxes). Minimum, maximum, average, median and various percentiles of the samples (P90, P50, P25, P10) were calculated from for the end-members assuming a log-normal distribution. The percentile 10 (P10) composition covers the elemental concentrations for which 10% of the samples is above. For the P25, 25% has elemental concentrations higher than the given values, etc. The resulting compositions are a part of the classification of the different water types used to study the potential risk of precipitation of solids (Section 3.4). The composition of the end-members is presented in Table 1 and a full account of the end-member statistics are presented in the Supplementary Material Table 1. Comments on the table with variations within same day, is shown in Supplementary Material Table 2.

EM1 is characterized by low-medium salinity, low  $\mathrm{Sr}^{2+}$  and high  $\mathrm{Ba}^{2+}$  contents. EM2 is similar to North Sea seawater (composition from The Danish Energy Agency (Danish Energy Agency, 2013)) and is characterized by medium salinity and high  $\mathrm{SO}_4^{2-}$  and  $\mathrm{Mg}^{2+}$  concentrations. EM1 and EM2 are found on the Halfdan and Dan fields. EM3 is characterized by medium-high salinity, high  $\mathrm{Ca}^{2+}$  and  $\mathrm{Sr}^{2+}$  and no Ba<sup>2+</sup> and is produced mainly on the Dan fields (and the Halfdan South field). EM4 represents the water produced at the Valdemar field and has very low salinity and high  $\mathrm{Ba}^{2+}$  concentrations. Lastly, EM5 represents the water found on the Kaka field and is characterized by high salinity, high  $\mathrm{Ca}^{2+}$  and  $\mathrm{Sr}^{2+}$ , and low  $\mathrm{Ba}^{2+}$  contents. It is noted that no differences between the water produced from the Tuxen and Upper Cretaceous formations on the Valdemar field are observed, despite the fact that these two reservoirs are not physically connected.

The composition of each end-member has been analyzed with the Extended UNIQUAC thermodynamic model to study the saturation levels. The determined saturation indices (SI) for NaCl, SrSO<sub>4</sub>, BaSO<sub>4</sub>, CaCO<sub>3</sub>, and CaSO<sub>4</sub> are given in the <u>Supplementary Material Tables 3–6</u>. It is found that the end-members all are associated with a risk of precipitation of CaCO<sub>3</sub> and BaSO<sub>4</sub>. EM3 and EM5 also show a risk of SrSO<sub>4</sub> precipitation. This is discussed in details in Section 5.3.

#### 4.4. Elemental variations

In order to illustrate the geochemical variation in the data, the correlation between the following ions pairs has been tested by cross-plotting: Na<sup>+</sup> vs. K<sup>+</sup>, SO<sub>4</sub><sup>2-</sup> vs. Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> vs. Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> vs. Ba<sup>2+</sup>, Ba<sup>2+</sup> vs. Cl<sup>-</sup>, Ca<sup>2+</sup> vs. Cl<sup>-</sup>, Mg<sup>2+</sup> vs. Ca<sup>2+</sup>, Mg<sup>2+</sup> vs. SO<sub>4</sub><sup>2-</sup> and Sr<sup>2+</sup> vs. SO<sub>4</sub><sup>2-</sup>, since these most clearly illustrate the transition in water types. The variations are shown in Fig. 5 for SO<sub>4</sub><sup>2-</sup> vs. Cl<sup>-</sup>, Ca<sup>2+</sup> vs. Cl<sup>-</sup>, Mg<sup>2+</sup> vs. Ca<sup>2+</sup>, and Sr<sup>2+</sup> vs. Ca<sup>2+</sup>, and Sr<sup>2+</sup> vs. SO<sub>4</sub><sup>2-</sup> and Fig. 6 for Na<sup>+</sup> vs. K<sup>+</sup>. The remaining cross-plots are shown in the Supplementary Material Fig. 12.

#### 4.4.1. Chloride and sulphate

In a  $SO_4^{2-}$  vs. Cl<sup>-</sup> diagram (Fig. 5A), the data from the fields show distinctly different groupings. The Cl<sup>-</sup> concentration ranges from 13000 mg/L to 75000 mg/L and  $SO_4^{2-}$  ranges from 0 mg/L to 3800 mg/L. Samples from the Kraka field define a rather tight group characterized by relative high Cl<sup>-</sup> concentrations (60000–75000 mg/L) and mediumlow  $SO_4^{2-}$  concentrations (2060 mg/L). The samples from the Valdemar field have low and Cl<sup>-</sup> concentrations with relative small variance (13000–31000 mg/L) and low-medium  $SO_4^{2-}$  concentrations (0–1200 mg/L), with the exception of a few samples, which plot away from the fields.

Samples from the Dan and Halfdan fields overlap and plot between the Kraka and the Valdemar fields. They extend out towards a composition that matches the injected seawater (19350 mg/L Cl<sup>-</sup> and 2710 mg/L SO<sub>4</sub><sup>2-</sup>). It is, however, significant that a substantial overlap between the Halfdan and Dan fields is generally observed, although, with a few exceptions: A group of the Dan wells have a lower SO<sub>4</sub><sup>2-</sup> concentration for a given Cl<sup>-</sup> concentration compared to samples from the Halfdan field, suggesting that part of the water from Dan is compositional different than water from the Halfdan field.

We interpret the Cl<sup>-</sup> and SO<sup>2</sup><sub>4</sub> variations (Fig. 5A) to reflect the difference in the composition of the initial water types, which are modified over time with injected water and added production related chemicals. The highly saline water in the Kraka field, thus, reflects the field's structural position atop a Zechstein salt dome combined with the fractured nature of the reservoir. The low salinity in the Valdemar field, on the other hand, reflects the field's structural position on an inversion ridge geographically separated from mobile salt in the sub-surface. The effects of the production strategies applied on the four fields provide additional variation in the data. The water flooded Dan and Halfdan fields are highly altered. A few samples contain SO<sup>2</sup><sub>4</sub> in concentrations higher than what is present in seawater (with up to 40% higher). This is



**Fig. 5.** Cross-plot of A)  $Cl^-$  and  $SO_4^{2-}$ , B)  $Sr^{2+}$  and  $SO_4^{2-}$ , C)  $Cl^-$  and  $Ca^{2+}$ , and D)  $Mg^{2+}$  and  $Ca^{2+}$ . The arrows illustrate the main trends, which are discussed in the text. The squared boxes represent the five localized end-members (EM). These are defined in Table 1.

most likely due to  $O_2$  scavenging chemicals being added to the reservoir through the injected water, typically as  $Na_2SO_3$ . The injected  $SO_3^{2-}$  is oxidized into  $SO_4^{2-}$  inside the reservoir, and, thus, present as  $SO_4^{2-}$  in the produced water (CECA Arkema Group, 2019; Kelland, 2014).

### 4.4.2. Strontium and sulphate

The sample groupings in the  $\mathrm{Sr}^{2+}$  vs.  $\mathrm{SO}_4^{2-}$  diagram (Fig. 5B) follow the same overall patterns as outlined above: the Valdemar field has the lowest levels of  $SO_4^{2-}$ , followed by the Halfdan, Dan fields and, lastly, the Kraka field, which shows the highest levels of both  $SO_4^{2-}$  and  $Sr^{2+}$ . The Sr<sup>2+</sup> level details the PWC differences, particularly, between the Dan and Halfdan fields, where the Dan field displays higher levels than the Halfdan field. For the whole data set the  $Sr^{2+}$  level ranges from 0 mg/L to 520 mg/L. The low levels are typically found in seawater-influenced produced water due to the increasing risk of precipitation of SrSO<sub>4</sub> at increasing  $SO_4^{2-}$  concentrations. The  $Sr^{2+}$  source is most likely dissolution of Sr<sup>2+</sup>-bearing minerals within the Zechstein salt diapirs as the highest concentrations are found in the Kraka field and the lowest concentrations in the fields not associated with salt. However, it is interesting to note that the  $\mathrm{Sr}^{2+}$  concentrations do show an overlap between the Kraka and Dan fields. Similarly, these fields do not display identical Cl<sup>-</sup> concentrations (Fig. 5A and C), which suggests the two are not connected.

One may suspect that the upper line of the  $Sr^{2+}$  vs.  $SO_4^{2-}$  cross-plot is determined by the potential precipitation of  $SrSO_4$ . Calculations in Extended UNIQUAC support this suggestion. The compositions of four

points on the upper line of the plot were tested with Extended UNI-QUAC. The calculations were carried out at reservoir conditions, ambient conditions, and cool storage conditions. In the calculations, we have used the composition of seawater (given by The Danish Energy Agency (Danish Energy Agency, 2013)) with increased  $\text{Sr}^{2+}$  and  $\text{SO}_4^{2-}$  concentrations to match the levels in the cross-plot. For all tested compositions, super saturation of  $\text{SrSO}_4$  is predicted; that is, precipitation of  $\text{SrSO}_4$  (0.3–1.2 g) is possible. See Supplementary Material Table 7 for further details. For pure seawater, the saturation index of  $\text{SrSO}_4$  is found to be 0.610 and 0.463 at reservoir and ambient conditions, respectively. Hence, it is below the saturation limit.

#### 4.4.3. Chloride and calcium

The sample groupings in the Cl<sup>-</sup> vs. Ca<sup>2+</sup> and Mg<sup>2+</sup> vs. Ca<sup>2+</sup> plots (Fig. 5C and D, respectively) illustrate aspects related to the reactivity of the chalk itself. The Ca<sup>2+</sup> concentrations range up to 10 000 mg/L with peak values measured both in samples from the Valdemar, Dan and Halfdan fields. The high Ca<sup>2+</sup> concentrations in these wells mostly stem from the first years of production, indicating these high levels may be found in formation water. Furthermore, completion fluids (containing CaCl<sub>2</sub>) and acid stimulation treatments may have contributed to the high Ca<sup>2+</sup> concentrations are also seen on the time series diagrams presented in Fig. 3. As in Section 4.4.1, a distinction between the four fields is observed on the Cl<sup>-</sup>-axis caused by increasing salinity.

#### 4.4.4. Magnesium and calcium

In the  $Mg^{2+}$  vs.  $Ca^{2+}$  plot (Fig. 5D), several trends are observed.  $Mg^{2+}$  concentrations up to 1550 mg/L are observed at low  $Ca^{2+}$  values. This trend most likely reflects that seawater is being mixed with formation water and is, as expected, typically observed at the Dan and Halfdan fields. This observation is confirmed by the time plot shown in Fig. 3. A second trend is seen at high  $Ca^{2+}$  concentrations (up to 10 000 mg/L), which seem to correlate with low  $Mg^{2+}$  concentrations. This trend may be caused by a number of factors: 1) The influence of completion fluids, notably acid treatment, 2) the contribution of  $Ca^{2+}$ from the chalk itself, and 3) cation exchange of  $Mg^{2+}$  and  $Ca^{2+}$  between water and the chalk surface.

In the intermediate region between the Dan and the Halfdan fields, the Kraka and the Valdemar fields plot with an approximate 1:5 ratio between  $Mg^{2+}$  and  $Ca^{2+}$  probably reflecting the original low  $Mg^{2+}$ content of the chalk (calcite). Generally, the  $Ca^{2+}$  concentration is lower in water produced from the Halfdan field than from the Dan field. Both Halfdan and Dan produce water with  $Ca^{2+}$  and  $Mg^{2+}$  concentrations similar to those found in seawater, which is relatively high in  $Mg^{2+}$ . A group of the Halfdan samples point towards high  $Ca^{2+}$  concentrations; this group consists of samples from different wells, all from the first twothree years of production. This indicates that the  $Ca^{2+}$  level is affected by the completion of the well. The samples from the Kraka field display a clear  $Mg^{2+}:Ca^{2+}$  ratio trend of 1:5. The samples deviating from this trend are all from the very beginning of the production. Again, this indicates that these early samples are affected by the completion fluids.

A similar plot as Fig. 5D, but with time added as a factor, shows that at the beginning of the production, extremely high Ca<sup>2+</sup> concentrations (up to 10 000 mg/L) are observed, but these even out with time and after three years of production, none of the produced water samples contain  $Ca^{2+}$  in concentrations higher than 2000 mg/L. The high  $Ca^{2+}$  concentrations most likely stem from acid treatments or enhanced carbonate dissolution related to near well compaction and pressure dissolution at production start. The variance in the  $Mg^{2+}$  levels is evenly distributed in time. Cation exchange of  $Mg^{2+}$  and  $Ca^{2+}$  inside reservoirs has been examined previously (Andersson et al., 2016; Farajzadeh et al., 2017; Bonto et al., 2019). An expected outcome of the exchange is that the  $Mg^{2+}$  concentration in the produced water decreases and the  $Ca^{2+}$ concentration increases with time. This trend is not clearly displayed in our data, hence, we conclude that conclusions may be difficult to draw upon PWC data and that detailed studies of the exact exchange mechanisms are necessary. Precipitation of magnesium containing minerals may be another explanation for the observed variance.

### 4.4.5. Sodium and potassium

The contamination by completion fluids and, especially, drilling mud that enters the formation when wells are drilled is especially evident on a Na<sup>+</sup> vs. K<sup>+</sup> plot (shown in Fig. 6) since a K<sup>+</sup>-rich mud system typically was applied during drilling. In the data,  $K^+$  values as high as 5500 mg/L are measured at both the Valdemar, Halfdan and Dan fields, whereas, only one sample from the Kraka field shows elevated concentrations. All samples with elevated K<sup>+</sup> concentrations, according to our observations, are samples from the first few years of production. This confirms, the levels most likely are caused by contamination introduced upon completion of the wells. That only one sample from the Kraka field has elevated K<sup>+</sup> suggests that the Kraka field has been rather uncontaminated throughout the production. The spread on the Na<sup>+</sup>-axis is grouped into the different fields with the same sequence as for the  $Cl^-$  and  $Ca^{2+}$ values (from low to high): Valdemar, Halfdan, Dan and Kraka. This is what we expect, as it is known that the Kraka field is the most saline field and the Valdemar field the least saline. Na<sup>+</sup> is expected to decrease slowly as a result of seawater injection (Fig. 3). The level of back flow of the mud system will, among other things, depend on the chalk permeabilities. In low permeable chalk, we suspect, it takes the longest time for back flow and clean-up of the production stream compared to high permeable chalk. In this context, it is noted that the lowest permeable



**Fig. 6.** Cross-plot of Na<sup>+</sup> and K<sup>+</sup>. The Na<sup>+</sup> concentrations given in this plot are all estimates based on a neutral charge balance. The boxes represent the five localized end-members (EM). These are defined in Table 1.

chalk represented by the Lower Cretaceous Tuxen and Sola formations in the Valdemar field samples do appear more contaminated than the fractured chalk seen in the Ekofisk Formation on the Kraka field which supports the hypothesis. Additionally, very different stimulation and completion procedures have been applied to the different fields, which may affect the clean-up of the wells. Unfortunately, only a few samples from the Kraka field are available, hence, this cannot be examined in detail.

#### 4.5. Intra-field variations

The intra-field variations of the PWC are analyzed for the Halfdan and Dan fields (Figs. 8 and 9, respectively and Supplementary Material Figs. 8 and 9, respectively). The Halfdan field is divided into six sections: North East, North Central, North West, South East, South West and Spine; with the north and south referring to the spine of the field (sectioning shown in Fig. 10). The model includes only seven ions since Ba<sup>2+</sup> was removed from the analysis because it caused disordered model results (Martin-Fernandez et al., 2003; Buccianti and Pawlowsky-Glahn, 2005; Filzmoser et al., 2009a).

The PCA model of the Halfdan samples consists of 3668 samples. The first two axes of the model account for 93% of the total variance and the third principal component (PC-3) axis covers 4%. Hence, the first two PCs cover the variance entirely. The loading plot is roughly similar to that of the PCA model of the total data set (Fig. 4 and taken in consideration Ba<sup>2+</sup> is left out) and display a grouping of Na<sup>+</sup>, Cl<sup>-</sup> and Ca<sup>2+</sup> at positive PC-1 (weight  $\approx 0.2$ ). At low negative PC-1 and positive PC-2 a grouping of Mg<sup>2+</sup> and K<sup>+</sup> plots, SO4<sup>2-</sup> plots at high negative PC-1 and positive PC-2. On the PC-1 vs. PC-3 plot, Ca<sup>2+</sup> plots away from Na<sup>+</sup> and Cl<sup>-</sup>. Sr<sup>2+</sup> plots at high PC-1 and PC-2. The variation in the PC-1 axis is controlled similarly as in the model of all the data presented in Fig. 4 by low SO4<sup>2</sup>-saline water and high SO<sup>2-</sup>-low saline water identified as the injected seawater. The domination of Ca<sup>2+</sup> on the PC-3 most likely reflects the produced formation water and the effects induced by acid stimulation.

From the sample score plot, Fig. 7A, it is observed that samples from South West region plot around the origin. This indicates that the Na<sup>+</sup>-Cl<sup>-</sup> component is prominent and suggests that the most saline water is produced in this part of the field. Samples from North East plot away



Fig. 7. PCA of PWC from the Halfdan field. The colors reflect the geographical location of the sample. A) Score plot and B) loading plot of PC-1 vs. PC-2 axis.



Fig. 8. PCA of PWC from the Dan field divided into two geographically defined groups: Northwestern (NW) flank and the Central Dome (CD). A) PCA score plot and B) PCA loading plot of PC-1 vs. PC-2 axis.

from the  $SO_4^{2-}$  loading, suggesting this part of the field has the "weakest"  $SO_4^{2-}$  component and thus, is the least affected by seawater injection. North Central and North West plot on top of each other and display the largest overall spread.

The wells from the Dan field have been divided into two groups: Wells from the Northwestern (NW) flank facing the Halfdan field and the remaining wells that are situated on Central Dan. The model includes in total 4895 samples. The two first components of the PCA model (PC-1 and PC-2) cover 88% of the total variance. This model includes only seven ions since  $\mathrm{Ba}^{2+}$  was removed from the analysis because it caused disorder (Martin-Fernandez et al., 2003; Buccianti and Pawlowsky-Glahn, 2005; Filzmoser et al., 2009a). The PC-1 loading plot depicts the two groupings of elements previously recognized of the PCA model, which consist of Cl<sup>-</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, and Sr<sup>2+</sup> at increasing positive PC-1 values; and  $K^+$ ,  $Mg^{2+}$  and  $SO_4^{2-}$  at increasing negative PC-1 values, respectively. This trend is interpreted to reflect seawater (high negative) to formation water (high positive). On the PC-2 axis, K<sup>+</sup> plots at high negative values together with Ca<sup>2+</sup>. This component is interpreted to reflect stimulation fluids and/or mud contamination, which are typically characterized by high  $K^+$  and associated with high  $Ca^{2+}$  as discussed previously.

The score plot of the samples (Fig. 8A) show that the wells from Central Dan exhibit the largest span in PC-1 and PC-2 values, whereas, the samples from the wells on the Northwestern flank plots more localized. In terms of water chemistry this reflects that the Northwestern flank both produces water with less extreme salinities and  $SO_4^{2-}$  levels than wells from the Central Dome itself. Furthermore, the samples from the Northwestern flank appear to be much less influenced by completion fluids and other contaminants than the wells on the Central Dome. The Northwestern flank was developed somewhat late in the field history. The wells here have, thus, been water flooded for a shorter time than the remaining wells, which might explain the difference in the seawater component between the two groups on the Dan field. The different development stages between the Northwestern flank and the remaining wells may also explain the difference in completion fluids in the produced water, suggesting that completion strategies may have shifted during development. However, that lack of high saline water in the Northwestern flank suggests that water types vary across the field.

The data from the Kraka and Valdemar fields is very sparse and does not allow for a similar discussion.



Fig. 9. Regional changes in the water composition across all four fields. A) PCA score plot and B) PCA loading plot of the PC-1 and PC-2 axis. The boxes represent the five localized end-members (EM1-EM5). These are defined in Table 1.

#### 4.6. Inter-fields variations

Fig. 9 shows the plot of PC-1 vs. PC-2 for all four fields collected in one analysis (Fig. 9 is a plot of the same data presented in Fig. 4, but with a different color coding.). Generally, great similarities in the composition of the produced water at the Halfdan and Dan fields are observed. This suggests that the water either has the same origin or that the water migrates through the fields and, hence, that the two fields are connected. A group of samples from the Dan field are found to have a composition not found on the Halfdan field. These samples are all from the Dan Central Dome. The Valdemar field plots distinctly separate from the other fields. It has a strong positive  $Ba^{2+}$  component and strong negative  $SO_4^{2-}$  component. This observation is confirmed by the PC-2 vs. PC-3 plot (Supplementary Material Fig. 10).

Here an additional strong K<sup>+</sup> component is displayed. All these factors suggest that the Valdemar field is greatly influenced by completion fluids and has a Ba<sup>2+</sup> profile distinctively different than the other fields, which is in agreement with observations presented earlier in this paper (Figs. 3 and 4). The samples from the Kraka field all plot closely together, suggesting that the Kraka field produces a very homogeneous water. The field has a significant Na<sup>+</sup>-Cl<sup>-</sup>-Sr<sup>2+</sup> component, which confirms a larger variance in Na<sup>+</sup>-Cl<sup>-</sup>-Sr<sup>2+</sup> observed for the highly saline water at the Kraka field. These observations are confirmed by the PC-1 vs. PC-3, PC-2 and PC-3 plots, both shown in the Supplementary Material Fig. 10.

#### 5. Discussion

The water produced from an oil well is a mix of natural occurring substances, directly added chemicals and substances related to the construction of the well itself. Throughout our analysis, it has been observed that the data is indeed affected by a multitude of processes. However, by the use of multicomponent data analysis these effects can be sorted out and subsurface patterns can be analyzed. So far, we have presented the compositions of produced formation water and analyzed them across different variables. In the following a brief discussion of the influencing factors on the compositions is presented, followed by an outline of the geological and production related implications.

#### 5.1. Factors influencing the produced water composition

The data presented in this paper stems from chemical analysis of produced water samples. The aim of the chemical analysis is to accurately determine the ionic composition of the given samples. It is known that some uncertainty is associated with this analysis, and the samples themselves carry a significant uncertainty due to varying quality of sampling procedures, post-production treatment and storage. The water produced from the fields is directly influenced by injected chemicals, e.g. from drilling mud, O2 and scale inhibitors, squeeze events, re-stimulation and well clean-ups. The impact on the PWC is observed as back flow of the injected chemicals. Hence, the effects are typically greatest on the samples from the first five years of production (Schovsbo et al., 2017, 2018). Above, it was shown that after ten years of production, the Na<sup>+</sup>-Cl<sup>-</sup>-Sr<sup>2+</sup>(-Ca<sup>2+</sup>) component in the PCA plot was less strong than in the first ten years of production. This suggests that the concentration of these ions stabilizes over time. Also, it has been found that the  $Mg^{2+}$ -  $SO_4^{2-}$  component is the strongest component, which reflects the impact of the injected water, which is known to contain high levels of Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>. It should be noted that the sulphate is currently not removed from the injection water on any of the Danish North Sea fields. This is generally done in order to prevent excessive reservoir souring caused by the metabolism of sulphate reducing bacteria of SO<sub>4</sub><sup>2–</sup> to H<sub>2</sub>S which causes many problems in oil production including safety risks (Larsen et al., 2004; Mitchell et al., 2010).

A reservoir's capability to clean up is highly dependent on its permeability and initial oil saturation. A high permeability and a low oil saturation will provide the best conditions for fast clean up caused by higher flow rates and dilution of chemical signature by formation water. Overall, the Lower Cretaceous Sola and Tuxen formations in the Valdemar field have low permeability. The Upper Cretaceous Tor formations in the Dan and Halfdan fields have higher permeabilities and the Paleogene Ekofisk Formation (the Valdemar field) has the highest effective permeability due to the fractured nature of the reservoir. The Halfdan field has a high oil saturation in the producing zones (up to 97%) (Albrechtsen et al., 2001). Thus, it is expected that the Halfdan and the Valdemar fields need years to fully clean up after completion, which is in agreement with our observations (Figs. 3 and 4). Previously, it was shown that the Kraka field is nearly non-affected by completion fluids, which indicates a very efficient clean up ability (Fig. 6).

The measurements of  $Ba^{2+}$  and  $Sr^{2+}$  contain a lot of uncertainty because their concentrations are closer than the main ions to the experimental lower limit of detection (LOD). For  $Ba^{2+}$ , the concentration is may be lower than the LOD. In these cases, the concentration is not reported. Thus, our data is rather incomplete with respect to  $Ba^{2+}$ . The LOD reported to us by the operator is 1 mg/L, hence, in the lack of a better estimate, we set the missing values to 1 mg/L. In the detailed PCA

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of the Halfdan and Dan fields, we have left the Ba<sup>2+</sup> concentration out to minimize the uncertainty of the results (Aitchison, 1986; Martin-Fernandez et al., 2003).

The addition of acid to the sample immediately after sampling supports the supersaturation at ambient and cool storage (acid has not yet been added while the sample is under reservoir conditions). From the calculated SI (Section 3.4 and Supplementary Material Tables 3–6), it is found that the produced water is indeed supersaturated with respect to some of the relevant salts. This suggests that some of the "original information" is stored in the samples, and the addition of acid immediately after sampling helps preventing precipitation despite the produced water may be supersaturated with respect to some salts.

#### 5.2. Injection water breakthrough

Routinely,  $SO_4^{2^-}$  is used as marker for injection breakthrough of injection water, which contains high amounts compared to the formation water originally present in the reservoir. (McCartney et al., 2005; Vazquez et al., 2015). In some fields, the Cl<sup>-</sup> concentrations in formation water and injection waters differ only very little and may not be used as tracer for injection water breakthrough. In our study, the Cl<sup>-</sup> and  $SO_4^{2^-}$  concentrations differ greatly between formation water and injection water. Consequently, both appear to be effective tracers of injection water. Additionally, we show that  $Mg^{2+}$  and  $Ca^{2+}$  follows a general pattern;  $Mg^{2+}$  increases and  $Ca^{2+}$  decreases, until the time of injection water breakthrough, where they both stabilize. Hence, we can suggest that the concentration of these two ions in combination with Na<sup>+</sup>, Cl<sup>-</sup> and  $SO_4^{2-}$  is used as a multi-elemental marker for injection water breakthrough. This provides a more robust method for identifying injection water breakthrough.

#### 5.3. Scale and corrosion

In Danish chalk fields scale types including the hard, insoluble scales  $BaSO_4$  and  $SrSO_4$  and the soft scales such as iron scales (Fe(OH)<sub>2</sub>, Fe (OH)<sub>3</sub> and others) and CaCO<sub>3</sub> have been identified (Puntervold et al., 2009; Shaw et al., 2010, 2012; Amiri et al., 2013; Jimoh et al., 2017). The prediction of scale formation complicated by the fact that it is dependent on many parameters such as local temperatures and flows, the ionic concentrations and pH. The most used indicator of scale potential is still the concentration of ions measured in the water at the wellhead. In many oil fields in the Danish North Sea, including the Halfdan field, scale has proven to be a significant risk in some wells (Jones et al., 2006).

The Ba<sup>2+</sup> and Sr<sup>2+</sup> concentrations and even slight variations therein are very important for the monitoring and mitigation of the potential formation of insoluble scales in the presence of SO<sub>4</sub><sup>2-</sup> (Puntervold et al., 2009). SrSO<sub>4</sub> and BaSO<sub>4</sub> are critical when formed in the wellbore area, while they are less harmful overall when deposited in the reservoir (Jones et al., 2006). Water flooded reservoirs, such as the Halfdan and Dan fields, are more sensitive as the injection water introduces large amounts of SO<sub>4</sub><sup>2-</sup>.

The high  $Ba^{2+}$  concentrations, observed at Halfdan and Valdemar, occur independent of gas content and are seen in these two fields and in oil northerly chalk fields such as South Arne but also in Paleocene sand fields in the Siri canyon, just to mention the occurrence in Danish Central graben (Schovsbo et al., 2016).

The water compositions of the end-members presented in this paper have been tested by the Extended UNIQUAC thermodynamic model, which can give an indication of the risk of scale precipitation (with emphasis on CaCO<sub>3</sub>, BaSO<sub>4</sub> and SrSO<sub>4</sub>) by calculating the saturation indices of salts in solution at a given temperature and pressure. The results are presented in Supplementary Material Tables 3–6. From the calculations, it is found that the end-members (EM) are all supersaturated with respect to CaCO<sub>3</sub> and BaSO<sub>4</sub> at all conditions. It is shown that EM4 (the Valdemar field) is the most sensitive to BaSO<sub>4</sub> formation, followed by EM1 (the Halfdan North field). This is explained by the high  $Ba^{2+}$  levels present in the reservoirs. All end-members are supersaturated with respect to CaCO<sub>3</sub> at all conditions. EM3 (Dan and Halfdan South) and EM5 (Kraka) are supersaturated the most. SrSO<sub>4</sub> is found to be critical for EM3 (Dan and Halfdan South) and EM5 (Kraka) and at reservoir conditions only. Hence, it is not expected to be present in the wellbore area, which is the most critical place (Jones et al., 2006).

The Extended UNIQUAC calculations are carried out with the mean compositions and the P10 compositions of the EMs. The observed trends are similar for the two modelled compositions; they are simply stronger with the P10 compositions (Supplementary Material Tables 4 and 6). The produced water is supersaturated with respect to CaCO<sub>3</sub>, BaSO<sub>4</sub> and SrSO<sub>4</sub> because it may not have reached equilibrium upon the time of production due to the high production rate. Furthermore, acid is added to the samples immediately after sampling, which supports the supersaturation (the solubility is expected to be higher in a charged solution).

Extended UNIQUAC calculations have also been carried out with compositions of the end-members (EMX; X = 1, 3, 4, 5) mixed with endmember 2 (EM2). EM2 is representative of the injected water after equilibration with the reservoir and is, thus, more relevant to use as model composition than pure seawater. The examined mixtures consist of 40% EMX and 60% EM2 to model a representative mixing situation between formation water and injection water. The results are given in Supplementary Material Tables 5–6. The observed trends are similar to those found for the pure EMs although the mixtures are closer to saturation or are predicted to be supersaturated with respect to the sulphate salts (BaSO<sub>4</sub>, SrSO<sub>4</sub> and CaSO<sub>4</sub>). This is as expected, because the injected water (EM2) contains a high amount of SO<sub>4</sub><sup>2–</sup>, rarely found naturally in the reservoirs. Furthermore, we find that the sensitivity towards CaCO<sub>3</sub> scale formation is decreased.

Unfortunately, the iron content [Fe(II) and Fe(III)] is not available to us and we can, thus, not evaluate the risk of iron scales. Measurements of water pH immediately after sampling would also be a helpful parameter to improve the robustness of the model, however, this is unfortunately not available in this data set either.

#### 5.4. Fluid dynamics in the Halfdan-Dan area

Direct evidence of fluid movement in the chalk has not been found. However, based on the reservoir pressure distribution and detailed structural modelling of the Halfdan-Dan area Albrechtsen et al. proposed that hydrodynamic forces drive the water towards southwest in the Halfdan field due to tilting of the area (Albrechtsen et al., 2001). According to this model (Fig. 10), the water is expelled from the Sif and Igor area located northeast of the Halfdan field due to the tilting of the area.

Hydrodynamic flow of water has also been inferred by Vejbæk et al. (2005). According to their study the water in the Halfdan field began to flow approximately seven million years ago. The pressure data suggests an average flow rate of 2 km/Ma, corresponding to a travelled distance of 14 km (Vejbæk et al., 2005). These rates and distances imply that the water from the Halfdan field have passed through the Dan field by now. Again, this observation fits the presented data related to the general increase in salinity from the eastern part of the Halfdan field across the Dan Northwest field and to central parts of Dan. As an alternative explanation to fluid movements as the main cause for water type differences is passive diffusion of ions, notable Cl<sup>-</sup> from the subsurface Zechstein salt. Accordingly, the shift differences in water types is expected to mimic the subsurface structure of salt with local maximum around local fracture aiding flow of deep salt brines. The presence of salt domes and pillows undoubtedly places a first order control on the salinity in the Danish North Sea. The high salinity water found on the Kraka field and the central part of the Dan field is a direct reflection of this. With respect to the Halfdan field, the higher Cl<sup>-</sup>, which are found in the western part, may reflect the Skjold or Gorm salt domes, as a similar structure is absent on the eastern part of the Halfdan field. The salinity



**Fig. 10.** Flow model. Contour map of the top chalk (scale in feet) showing the Skjold-Halfdan-Dan-Igor area. The geographical division of the Halfdan (NE, NC, NW, SE, SW) and Dan (NW and CD) fields is shown with colored boxes. Relative fluid transport directions of oil, gas and water are from Albrechtsen et al. (Albrechtsen et al., 2001) The outline of the production well patterns are from the Danish Energy Agency (Danish Energy Agency, 2013). The median concentrations of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> for each area are in mg/L. The full median compositions are provided in Supplementary Material Table 8.

is, however, not the only parameter that influences the differences in the water types. The northeastern part of the Halfdan field is also distinguished by the content of other ions. Notably, high  $Ba^{2+}$  and low  $SO_4^{2-}$ , which suggests that the full ion picture of the ion concentration differences in the water types cannot be explained solely by subsurface salt and passive diffusion of ions.

With respect to our observation (Fig. 9), this implies that the  $Ba^{2+}$  rich low salinity water type (EM1), which is most clearly expressed in the northeast part of the Halfdan field, probably originates from the Sif-Igor area.

#### 5.5. Implications for production

The first phase of water injection in carbonate reservoirs has the purpose of maintaining the pressure inside the reservoir above the bubble point pressure and, thus, maintaining the physical sweep (Shehata et al., 2014). Later, the effect on the oil production has shown to be advantageous in some cases and interest in the mechanisms behind the effect of water injection on the mobility of fluids in the porous rock emerged. One mechanism of enhanced production is that seawater increases the oil recovery by spontaneous imbibition and viscous displacement (Austad et al., 2008). Many studies have indicated that the injection of seawater into a carbonate (chalk) reservoir has a positive effect on the oil recovery because it has the potential to alter the wettability of the rock (Austad et al., 2008; Puntervold and Austad, 2008; Puntervold et al., 2009, 2015; Shehata et al., 2014). In addition, the introduction of seawater can impact the compaction of the reservoir to induce a higher oil production, possibly via water weakening of the rock (Austad et al., 2008; Puntervold et al., 2009; Zangiabadi et al.,

2009). The mechanisms behind wettability changes are not completely understood. Some studies suggest that changes in total concentrations and concentration ratios of divalent ions in the water affects the adhesion of polar organic molecules to the rock (Zangiabadi et al., 2009; Puntervold et al., 2009, 2015; Shehata et al., 2014). As pure chalk is water wet in nature, the mixed wet behavior observed in chalk reservoirs is linked to the layers of material on the surface and the key to mobilize additional oil is in modification of these layers. This can also be achieved by costly solvent injection, but the more subtle effects of modifying injection water composition are of great interest. Thus, the field operators have an interest in monitoring and understanding the chemical composition of the water, and, ideally, in predictive modelling of these changes.

From the PCA, we have found and categorized five end-members. The salinity and the concentrations of the divalent cations which are the key ions considering the potential for enhanced recovery are the main parameters characterizing these five end-members (Table 1). Puntervold, Strand, and Austad have proposed an optimal concentration ratio of the determining ions to obtain the best possible recovery:  $Mg^{2+} \approx 2 \cdot SO_4^{2-} \approx 4 \cdot Ca^{2+}$  (Puntervold et al., 2009). This relative composition is not found in any of the end-members, suggesting the injection water can be further optimized to improve the recovery.

Other studies have demonstrated the effect of dilution of the injection water, both in sandstone and carbonate reservoirs.

#### 6. Conclusions

This paper presents an extensive analysis of produced water chemistry from the Dan, Halfdan, Valdemar and Kraka fields in the Danish

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North Sea. 8579 out of a total of 8749 samples are included in a multivariate statistical analysis. The produced water both reflects subsurface geology, fluid migration, applied production strategies and time effects.

The produced water itself is a mix of natural occurring substances, chemicals added to the injected water (relevant for the Halfdan and Dan fields) and substances related to the construction of the well itself. A clear strategy for data quality and contamination evaluation procedures have been applied. High K<sup>+</sup> values reflect contamination from completion fluids. The clean up time is correlated to the permeability of the fields; with Kraka being the field that is cleaned the fastest and Valdemar the slowest. Further valuable information could be gained from analysis of stable and radiogenic isotopes to gain deeper insights into the origin of the produced water.

Breakthrough of injection water can be identified, not only from the salinity and  $SO_4^-$  concentration, but also from a stable level of  $Mg^{2+}$  and  $Ca^{2+}$  at concentrations higher and lower than in the original formation water, respectively. This is observed at the Dan and Halfdan fields.

Five main water types are categorized: They differ greatly in salinity and in the concentration of the divalent ions (Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup>). The most saline water produced from the Kraka fields and the least saline water from the Valdemar field. The highest content of Ba<sup>2+</sup> is found on Valdemar.

The mapping of water across the four fields, up to 55 km apart from North to South, shows gradual changes in the composition reflecting regional scale hydrodynamics as well as subsurface geology. The presented data supports a fluid flow model where the Dan and Halfdan water is connected through time; the water from the Halfdan field has flown southwards through or by the Dan field.

Thermodynamic calculations using Extended UNIQUAC show that  $BaSO_4$  is potentially critical at particularly the Valdemar field, but also at the Halfdan and Dan fields;  $SrSO_4$  is potentially critical at the Kraka and Dan fields; and  $CaCO_3$  is expected to be supersaturated in the reservoirs in all the fields. Hence, scale formation is a concern at all the fields, based on the major ion concentrations available here For more accurate scale prediction, the pH, alkalinity and organic acid content of the produced water are required parameters which should ideally be included in all measurement protocols for produced water.

Our analysis has shown that data routinely collected by an industry for process control such as the produced water from Danish North Sea reservoirs contain valuable information on the subsurface process highly relevant for academia. However, knowledge gap of the data quality and lack of full geochemical analysis significantly hampers full usability of the data. For future analysis, full documentation of analytical procedures and analysis of especially pH, alkalinity and organic acids content will be valuable.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2020.104702.

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## A.2 Paper 2 Produced water from the North Sea - A case study and analytical guidelines

Contributions: Sofie N. Bergfors framed the study and developed the analytical workflow. Annette E. Jensen and Sofie N. Bergfors carried out the experimental work related to sample preparation and analysis. Sofie N. Bergfors analyzed the data and wrote the manuscript under the supervision of Simon I. Andersen and Karen L. Feilberg. All authors performed scientific and grammatical revisions of the final draft.

Figure captions are given in the end of the document, as requested by the journal.

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Produced water from the North Sea 1 - A case study and analytical guidelines 2 Sofie N. Bergfors\*, Simon I. Andersen, Karen L. Feilberg 3 4 5 The Technical University of Denmark, Center for Oil and Gas DTU, Elektrovej B375, 2800 Kgs. Lyngby, Denmark 6 7 8 \*sgott@dtu.dk 9 10 11 12 Abstract 13 The ionic composition (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>) of the 14 produced water has routinely been analyzed to follow injection water 15 breakthrough, monitor the performance and track potential scale precipitation 16 and corrosion in the wells. For the latter, the Sr2+ and Ba2+ (and SO42-) 17 concentrations are important to know accurately. Until now, IC has been applied 18 19 for the analysis. Often, Ba2+ is present in the samples in concentrations smaller than the LOD for the IC (1 mg/L). Hence, a more sensitive analytical technique is 20 21 22 23 24 25 26 27 needed for an accurate detection of Ba2+. Additionally, a sensitive analysis of eg. Ca2+ and Mg2+ and changes within, can support the understanding of cation exchange mechanisms. Furthermore, a well-documented workflow is crucial for accurate and interpretable results. Here, we present an analytical workflow for the handling and analysis of produced water samples combining Inductively Coupled Plasma - Optical Emission Spectroscopy and IC. The Halfdan field, located in the Danish North Sea, is used as case study for a comparison of experimental results. Generally, we find good agreement between reported data 28 29 and the presented analytical results. Most significantly, the new analytical LOD is 0.01 mg/L, which enables an accurate analysis of Ba<sup>2+</sup>. 30 31 32 33 34 35 Keywords: Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES), Ion 36 Chromatography (IC), Produced water chemistry (PWC), scale formation risk, water analysis. 37 38 39 40 41 42

## Introduction

Produced water is an unavoidable part of oil production. In the North Sea, the water cut starts at around 10 % v/v and reaches 40-50 % v/v after approximately 5 years. Several of the fields in the Danish North Sea are water injected. Here, the water cut may even reach >90% after 20 years in production. This is for example observed at the Dan field in the Danish North Sea. [1] Consequently, large volumes of water is produced. The produced water contains a wealth of information, some of which can be released by chemical analysis of the produced water. This information can be used to "significantly impact field economics", as stated by Schlumberger. [2] The produced water chemistry (PWC) informs the choice of production strategy, materials, water handling strategy and scale inhibition strategies. [3, 4] Moreover, in recent year, more attention has been paid to discharge strategies and the potential for re-injection of produced water. Not only for economical reasons, but also to protect the surrounding marine environment from the potentially toxic produced water. [5]

At the beginning of a well's life, the produced water is reflecting the *in-situ* formation water originally present in the reservoir. Formation water is characterized by a high  $Ca^{2+}$  concentration (up to 2500 mg/L) as the reservoirs in the North Sea are mainly composed by calcite, high salinity (total dissolved salinity (TDS) >40 g/L) and, for some fields, high  $Sr^{2+}$  and  $Ba^{2+}$  levels (up to 400 mg/l and 10 mg/L, respectively). [6] The injected water is typically modified seawater (removal of O<sub>2</sub>, filtration and addition of production chemicals) characterized by relatively high sulphate levels (2700 mg/L). [3, 7, 8] The mixing of these two water types introduces a potentially high risk of scale formation, which is typically  $Sr^{2+}$  and  $Ba^{2+}$  sulphates.

A previous study of the PWC of four North Sea fields (Dan, Halfdan, Kraka and Valdemar) is published by Bergfors *et al.* [6] This study is based on PWC data that covers analyses of produced water from the very early stage of production (1972-2007) and up to and including 2015. The PWC data covers the concentration of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Cl<sup>-</sup>, and SO4<sup>2-</sup>. The produced water composition is not constant, but varies both temporally and regionally. These changes are discussed in details in the cited paper. [6] The regional variations occur both between fields and within the same field and reflect the complex interplay of processes and subsurface 3D hydrodynamics. [3, 9, 10, 11, 7]

Some of the most interesting ions to follow include  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ,  $Cl^-$ , and  $SO_4^{2-}$ . Routinely, decreased  $Cl^-$  and increased  $SO_4^{2-}$  concentrations are used as a marker for breakthrough of injection water. [12, 13, 14] Furthermore, the  $Cl^-$  concentration is used to study flow patterns and predicting the mixing front in reservoirs, because  $Cl^-$  is a relatively inert ion and the concentration of it in the produced water is measurably diluted upon (sea)water injection. [3, 7, 8]

The concentration of K<sup>+</sup> has proven to be a good marker for well contamination from completion fluids and, especially, drilling mud that enters the formation when the well is drilled. A time resolved series of the K<sup>+</sup> ion reveals the clean up ability of a well. Bergfors *et al.* found that the Halfdan and the Valdemar fields need years to fully clean up after completion, as oppose to the Kraka field that is nearly unaffected by completion fluids, indicating a very efficient clean up ability. [6] Studies suggest that cation exchange between Ca<sup>2+</sup> and Mg<sup>2+</sup> is a typical

mechanism proposed for enhanced oil recovery (EOR). [15, 16, 17, 8, 18, 19, 20, 21] This exchange can be followed in the produced water composition where a reverse correlation between the Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations is observed. [6]

The Ba<sup>2+</sup> and Sr<sup>2+</sup> concentrations, and variations therein, provide valuable input for scale monitoring and mitigation strategies. Upon the introduction of  $SO_4^{2-}$  with the injected (sea)water, BaSO<sub>4</sub> and SrSO<sub>4</sub> may precipitate. [15] These are hard, insoluble scales that are especially critical when formed in the wellbore area, and less harmful when deposited in the reservoir. [22, 12, 13, 15] An accurate analysis of Ba<sup>2+</sup> and Sr<sup>2+</sup> is, therefore, crucial for an accurate prediction of scale. Especially Ba<sup>2+</sup> may appear in very low concentrations (<1 mg/L) in the produced water. Earlier used analytical techniques could not detect Ba<sup>2+</sup> at these low levels because they were below the lower limit of detection (LOD). Thus, a more sensitive technique for the analysis of Ba<sup>2+</sup> is required for a stronger prediction of scale potential.

Whether, it is for economical reasons, in perspective of enhanced production, environmental considerations, or deeper geological understanding, the data upon which a study is being made must be accurate and trustworthy. The study by Bergfors et al. mentioned previously relies on historical data received from the field operator (presently TOTAL). [6] The quality of the data upon which the study was conducted has not been sufficiently assured, but, this study aims to do so. At the operators, the analysis of produced water has been carried out by ion chromatography (IC), and some very early analyses include titration.

This study presents a method for the analysis of produced water using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) covering the ions: Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup>, combined with IC analysis of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. One of the main advantages of ICP-OES, as compared to IC, is the ICP-OES's ability of multielement determinations. Analytical wavelengths range from 170 nm to 800 nm and, generally, an ICP-OES can handle the measurement of up to 30 elements in one sample and is well suited for high-salinity samples (up to 30% TDS), like the samples presented in this study. Furthermore, the LOD for ICP-OES is parts per billion ( $\mu$ g/L), whereas it is around parts per million (mg/L) for common IC analysis. Thus, ICP-OES provides a more sensitive technique, which is especially relevant for the analysis of Sr<sup>2+</sup> and Ba<sup>2+</sup>. Last, but definitely not least important, the time needed for the analysis of one sample using the ICP-OES is about a factor of ten shorter than the time needed for the analysis of one sample using the IC (excluding the time needed to start up the instruments). The work going into sample preparation is similar for the two methods. One major drawback of ICP-OES is that it analyzes only cations, whereas an IC can analyze both cations and anions. Independently of the analytical method chosen, the analysis of cations and anions must be done separately. The concentration of the anions (Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) in the samples are at mg/L level, whereas  $Ba^{2+}$  reaches  $\mu$ g/L levels, thus, making the combination of ICP-OES (for cations) and IC (for anions) extremely powerful for the analysis of the produced water (and alike) samples.

To provide accurate results, not only must the analytic technique be sensitive and accurate, also the sample preparation is of great importance. To meet this, we have introduced a new sampling technique for off-shore produced water samples, together with a simple sample preparation procedure. The herefrom produced analytical results are compared with results from previous analyses by the operator. Consequently, we carry out an inter-laboratory quality check. 3

 $\begin{array}{c}
1\\2\\3\\4\\5\\6\\7\\8\\9\\10\\11\\12\\13\end{array}$ 

In short, this paper presents a new experimental technique which combines ICP-OES with IC for the analysis of produced water samples. It is fully documented and covers both the sampling of produced water and the following analysis of the ionic composition of the produced water. The technique is presented along with an evaluation of the new and the old analytical techniques, shining light on the quality of the historical data. The new technique including ICP-OES provides the possibility to accurately measure the Ba<sup>2+</sup> concentrations, which are often below the previous LOD ( $\mu$ g/L level). An accurate determination of Ba<sup>2+</sup> is extremely valuable for the future mitigation of Ba<sup>2+</sup> scale formation. A series of comparative studies are presented; an overview of the full study is provided in Figure 1 and is presented in the following sections.



## 1.1 Case study: The Halfdan field

The Halfdan field, which is used as a case study in this work, is located in the Northern part of the Danish North Sea. The field was discovered in 1999 and started production within that same year. [23] The field has in total 38 oil producing wells, from which 27 are water injected. Seawater is applied as the injection water. [1] The field is very systematically developed, with the wells placed in an alternating pattern of km-long multistage horizontal water injector and producer wells (Figure 2). Fracture Aligned Sweep Technology (FAST) concept, developed by Mærsk Oil, is applied in the aim of maximum water sweep efficiency. [24] In 2014, the field produced 64.98 m.m<sup>3</sup> oil and 47.72 m.m<sup>3</sup> water, respectively. [1] This is a large volume of water, that has to be disposed or reused, hence, it is important to address the water.



Figure 2.

## 2 Materials and methods

## 2.1 Samples

The sample set covers two types of off-shore samples; Table 1 provides an overview of the samples, that are described in further details below.

	Operator New Samples (ONS)	DHRTC New Samples 7 (DNS)
Time of sampling	October 2017 to June 2018	June 2018 to March 2019
Time of analysis	December 2018	July 2018 to April 2019 9 (approximately one month after sampling) 10
Treatment	HCl and/or HNO <sub>3</sub>	None 11
Number of samples	71	61 12
Place of sampling	HBA (32), HBB (8), HDA (31)	HBA (28), HBB (8), HDA (25)
Note	Analyzed by field operator approximately one month after sampling (Operator New	Transported directly to13DHRTC after sampling.14
	Data). Samples collected at the	15
	operator's (Operator) storage location in November 2018.	16

## Table 1.

For decades, the analysis of the off-shore samples have been taking place in an analytical laboratory run by the field operator, TOTAL from 2019. They receive the off-shore samples at quarterly intervals, and analyze the samples within a week of arrival. The samples have been collected at the test separator at the production platforms following the protocol used by the oil field operator. Immediately after sampling, acid (HCl and/or HNO<sub>3</sub>) is added to the samples in order to limit the risk of solid precipitation in the samples and prevent bacterial activity. The samples are stored in 250 mL oil-resistant plastic bottles in a dark, ventilated room at room temperature (20-25 °C) and stored for one year from the time of sampling. In November 2018, part of these stored samples (ONS) and constitute the first set of samples. ONS include 71 samples from the Halfdan field distributed as follows: 32 from HBA, 8 from HBB, and 31 from HDA. Up to three samples from the same well, sampled at different times, exist; for some wells only singles or duplicates exist.

The second set of samples (DNS) covers 61 samples from 23 wells at the Halfdan field distributed as follows: 28 samples from HBA, 8 from HBB and 25 from HDA. This includes 7 sets of two samples from the same well sampled at different times (1-5 months apart). These were sampled, following a new revised sampling protocol, which imposed a set of restrictions to the offshore sampling procedure and the following handling of the samples. Thus, limiting the introduction of unknowns and contamination of any kind. First, the samples were all collected at the test separator following the procedure set by the operator similar to ONS. To the DNS,

no chemicals (eg. acid or scale inhibitor) have been added. All samples were collected and transported in 1L oil resistant plastic containers. During transport, the

DNS were stored at room temperature, in the dark. (Ideally, the samples should be stored cold, but this was not practically possible.) The samples were received in batches within one month after they were sampled. Upon the arrival to the DHRTC laboratory, the samples were registered, transferred to 1L blue cap bottles and stored in a refrigerator at 5°C. Within one week after arrival, the samples were analyzed the first time. The DNS have been sampled from mid June 2018 to mid March 2019.

For all samples (ONS and DNS), the field, well, and sampling point, sampling. For some samples, the time of sampling is also given.

## 2.2 Data

Figure 3.

Data from the analysis of inorganic ions in produced water (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> Ba<sup>2+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) from the Halfdan field has been included to allow for a comparison with the analytical results achieved in the DHRTC laboratory. The received data is referred to as OND (Operator New Data). This includes PWC data from 2015 up to and including 2019. A subset of this data has been chosen for this particular study. Only data of samples from wells matching the samples available for analysis in the DHRTC laboratory (DNS and ONS) are relevant. Furthermore, the sampling time must match that of the physical samples. In the data set, we have chosen to include the nearest six samples for each well, where possible; that is, three samples older and three samples younger than the physical sample. This is illustrated in Figure 3. The maximum time span in the data samples included for each well is two weeks. The final data set contains compositional data of 158 samples distributed over 17 unique wells. All data mentioned here stems from IC analysis of both cations and anions.





Elemental ion	Concentration	Primary	Secondary
	mg/L	analytical	analytical
		technique	technique
Na <sup>+</sup>	15 000 - 30 000	ICP-OES	IC
K+	100 - 400	ICP-OES	IC
Mg <sup>2+</sup>	200 - 1 200	ICP-OES	IC
Ca <sup>2+</sup>	400 - 1 400	ICP-OES	IC
Sr <sup>2+</sup>	50 - 300	ICP-OES	-
Ba <sup>2+</sup>	< 2 (- 40)	ICP-OES	-
Cl-	20 000 - 85 000	IC	-
$SO_{4}^{2-}$	100 - 400 (- 3 000)	IC	-

#### Table 2.

In the presented work, parity plots are used to compare the data and experimental results. In all plots, the one-to-one correlation is shown (dashed line). Additionally, the +/-25% deviations from the one-to-one correlation are marked (full line). In the data comparison and discussion, all points within the 25% deviation are included unless else is stated.

## 2.3 Reagents

All reagents were prepared using Milli-Q water with a resistivity no higher than 18.2 m $\Omega$ . The water was purified using a Milli –  $Q^{\text{®}}$  Advantage A10 Water Purification System.

## 2.4 Sample preparation

The samples are filtered using a  $0.2 \,\mu$ m nylon filter to remove particulate matter and a potential minor organic phase. After, the samples are diluted using Milli-Q water for the IC analysis and using 2% HNO<sub>3</sub> for the ICP-OES analysis. The dilution factors are given in Supplementary Material Table 1. The approximate composition of the samples are given in Table 2 together with a specification of the analytical technique(s) used for the analysis of each of the elements. Besides the ions mentioned in Table 2, the samples are expected to contain bromide, carbonate, iron, phosphorous and various organic compounds. Neither of these are included in the analyses as they are not expected to influence the analytical results significantly. In the IC analysis, the organic compounds are removed using a guard column and the non-analyte inorganic ions are either not retained in the IC column or present in concentrations low enough to not impact the analysis. The low concentrations diminishes the risk for ionization suppression or spectral interference of the inorganic ions in the ICP-OES analysis.

## 2.5 Inductively Coupled Plasma Optical Emission Spectroscopy

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) is used for the analysis of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> in the produced water samples. The instrument is an iCAP<sup>TM</sup> 7200 from Thermo Fischer Scientific. It uses an Echelle optical design and a Charge Injection Device (CID) solid-state detector to measure trace elemental concentrations in aqueous solutions. The CID detector is kept cold by thermoelectric cooling with a ThermoFlex<sup>™</sup> 900 recirculating chiller from Thermo Fischer Scientific. The ICP-OES is equipped with a concentric nebulizer and a cyclonic spray chamber. It is provided with pure Ar(g) (N6.0) for both purging and the plasma. The specific settings of the instrument is given in Supplementary Material Table 2. The ICP-OES is equipped with an ASX-560 autosampler from Teledyne CETAC Technologies. To prevent cross contamination of samples, the autosampler is covered with a plastic enclosure, which is under suction. This also protects the samples from potential contamination from the surrounding environment. All reagents and samples used in the ICP-OES analysis were prepared using 2% HNO<sub>3</sub>, prepared from a 70%, ACS reagent grade, HNO<sub>3</sub>. Both reagents and samples are kept in tightly closed containers, cooled (5°C) and in darkness. The plasma is fed with 5.0 Argon from AGA.

The analysis of the off-shore samples was divided into two. One analysis of the ions present in bulk (>100 mg/L): Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>, and one for the ions present in traces (<1 to 200 mg/L): Sr<sup>2+</sup> and Ba<sup>2+</sup>. The analytical wavelengths used in the ICP-OES analysis are chosen wisely to avoid spectral interference. All elements are analyzed using two wavelengths, which is standard procedure and functions as a quality control. Table 3 lists the wavelengths used in this work. The reported concentrations are determined at the primary wavelength.

The samples are highly saline which is especially challenging for ICP-OES analysis, where ionization suppression can cause disturbance in the results. Fortunately, simple dilution of the samples is easily done and minimizes the risk of ionization suppression, which is crucial for an accurate analysis. The samples are diluted 70-fold (by volume) prior to the ICP-OES analysis, reaching a TDS of 0.3-0.6 g/L. At this dilution factor, the lowest concentrated ion, Ba<sup>2+</sup>, reaches concentrations at  $\mu$ g/L-level, which are still possible to detect using the axial mode.

A four point calibration curve was used for ICP-OES analyses. The compositions of the calibrations standards are given in Supplementary Material Table 3. The calibration standards contain a high concentration of Na<sup>+</sup> to matrix match. All the standards used in the ICP-OES analysis (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup>) are of certified reference material grade, 10000 mg/L in 2-5% HNO<sub>3</sub>, from VWR. The calibration regressions are given in Supplementary Material Table 3 and range from 0.90 to 1.0.

Based on the historical data, discussed previously by Bergfors *et al.*, we expect only minor changes in the PWC, thus, allowing the use of the simple external standardization method. [6] An internal standard (IS) is used to correct for instrumental drift and variations in the system efficiency (spray chamber, nebulizer, plasma etc.) within one analysis. The internal standard (IS) is introduced

continuously to the sample before it enters the spray chamber through a Y-shaped joining piece. Following, the tube is shaped in a double loop to ensure full mix of the sample and the internal standard. For the analysis of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>, 50 mg/L Y<sup>2+</sup> is used; and for the analysis of Sr<sup>2+</sup> and Ba<sup>2+</sup>, 10 mg/L Sc<sup>2+</sup> is used. The IS solutions are prepared with 2% HNO<sub>3</sub>. The internal standard makes up ca. 20% of the total sample volume after mixing with the sample and, crucially, the amount of internal standard added to the sample is constant throughout the analysis. The internal standards (Y<sup>2+</sup> and Sc<sup>2+</sup>) are 1000 mg/L in 2-5% HNO<sub>3</sub> from VWR.

Multielement standard solution 3 for ICP from Sigma Aldrich and iCAP 6000 Multi Element test solution from Thermo Fischer Scientific are used for quality control (QC) for the cation analysis with ICP-OES. These were chosen because they provide the best match with the composition of the samples of the conventionally available standards. The daily performance is checked using a 2 mg/L Zn solution, prepared from TraceCERT<sup>®</sup>, 1000 mg/L Zn in 2% HNO3, from Thermo Fischer Scientific. All analyses are run in triplicates and the results given are an average of the three. Further details of the analysis is given in the Supplementary Material.

Elemental ion	Mode	Primary wavelength,	Secondary	
		nm	wavelength, nm	
Na <sup>+</sup>	Radial	589.592	818.326	
K+	Radial	280.270	285.213	
Mg <sup>2+</sup>	Radial	422.673	315.887	
Ca <sup>2+</sup>	Radial	766.490	769.896	
Y+	Radial	371.030	-	
Sr <sup>2+</sup>	Radial	407.771	421.552	
Sc <sup>2+</sup>	Radial	363.075	-	
Ba <sup>2+</sup>	Axial	455.403	493.409	
Sc <sup>2+</sup>	Axial	361.384	-	

Table 3.

## 2.6 Ion Chromatography

Ion Chromatography (IC) is used for the analysis of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-,</sup> as only cations can be analysed using ICP-OES. Also, we do inter-instrumental control analysis of the cations Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> using IC. The instrument is a Dionex IonPac<sup>TM</sup> AS22, RFIC<sup>TM</sup>, with a 4 x 250 mm column. It has an IonPac<sup>TM</sup> CG16-4m, RFIC<sup>TM</sup>, 4 x 50 mm guard column. The guard column servestoremove possible impurities and suspended solids in the sample, to avoid the risk of them reaching the analytical column. For the anion analysis the eluent contains 4.5 mM sodium carbonate and 1.5 mM sodium bicarbonate and is prepared from Dionex<sup>TM</sup> AS22 Eluent concentrate. For the cation analysis, 30 mM methanosulforic acid is used as eluent.

The IC standards (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>) are of certified reference material grade, 10000 mg/L in water, purchased from Sigma Aldrich. The calibration standards are all prepared to match the concentration levels in the samples and are

diluted using Milli-Q water. The composition of the calibration standards are given in Supplementary Material Table 4.

Dionex<sup>TM</sup>Combined Five Anion Standard (F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>) from Thermo Fischer was used as quality control (QC) for the anion analysis. For the cation analysis, no quality control was run, as the analysis already functions as a control for the ICP-OES analysis.

## 2.7 Thermodynamic modelling

Thermodynamic modelling has been carried out to calculate the potential for solid formation of carbonate and sulphate scales (CaCO<sub>3</sub>, CaSO<sub>4</sub>, SrSO<sub>4</sub> and BaSO<sub>4</sub>). The calculations have been carried out using ScaleCERE based on Extended UNIQUAC, which is a thermodynamic model designed for electrolyte solutions. [25] The model provides the saturation index (ionic activity product divided by the solubility product) of the solids that can potentially precipitate from the solution. A saturation index higher than one reveals a situation where precipitation of solids is thermodynamically possible, thus, there is a potential risk of scale formation. However, solid formation is not certain as other parameters affect the formation of solids. For example kinetics, flow patterns in the wells and sticking factor of the surface. The ScaleCERE model is described in details elsewhere by K. Thomsen. [25, 28] The calculations are carried out at three different conditions: Reservoir conditions, ambient conditions and cool storage conditions. The conditions are described in details elsewhere. [6]

## Results

## 3.1 Sample composition: Operator New Data

The average composition of the produced water from a specific well at a time similar to the available DNS is calculated from OND. The calculated average compositions, together with the standard deviations and the number of samples used in the calculations, are given in Supplementary Material Tables 6-9 and are also shown in Figure 4. Some wells display significantly larger standard deviations than other. Two reasons for this are proposed: 1) The composition of the produced water is very unstable within the included time interval, or 2) instability in the analytical technique causes fluctuations in the results. The data stems from PW samples that are sampled maximum 8 months apart, consequently, smaller changes in the composition may appear. [6] Therefore, the variance in the data (large standard deviations) is interpreted as an indication of less reliable results.

Relative to the average concentration, the discrepancy is especially large for  $Ba^{2+}$ , which suggests that the external analysis of  $Ba^{2+}$  carries a large uncertainty. Also, the  $SO_4^{2-}$  concentrations show large relative standard deviations.  $SO_4^{2-}$  is involved in various reactions, here amongst others microbiological activity (sulphate reducing bacteria) and sulphate scale formation. These may affect the  $SO_4^{2-}$ concentration even after the sample has been collected.  $Na^+$ ,  $K^+$ ,  $Mg^{2+}$  and  $Ca^{2+}$ show the most consistent results. These are the cations present in the highest concentrations, thus making them the easiest to detect using IC.

Some general trends in the PWC observed include: Halfdan Northeast (NE) has high Ba<sup>2+</sup> levels and low SO<sub>4</sub><sup>2-</sup> levels. Water produced from Halfdan North Central (NC) is found to have low Ba<sup>2+</sup> concentrations. Halfdan Southeast (SE), Northwest (NW) and Southwest (SW) all display a high level of SO<sub>4</sub><sup>2-</sup>. This is in agreement with the observed trends presented by Bergfors *et al.* [6]
 **3.2 Comparison of experimental results and received data**The experimentally determined compositions of DHRTC New Samples [DNS] (determined using ICP-OES (cations) combined with IC (anions)) are given in

(determined using ICP-OES (cations) combined with IC (anions)) are given in Supplementary Material Table 5 and the average compositions determined from Operator New Data [OND] (determined using only IC) are given in Supplementary Material Tables 6-9. Figure 4 and 5 compare OND with the experimental results of DNS. Overall, good agreement between OND and DNS is observed. A large standard deviation in OND correlates with a large difference between OND and DNS. We argue, this proves that the difference is caused by an error in OND rather than in DNS, suggesting that the DNS results are more reliable.



Experimental analysis of DNS
 Average of similar samples, incl. one std.dev.

Figure 4.

Table 4 lists the trendslines and their regression coefficients for the parity plots shown in Figure 5. Points within $+/-25\%$ deviation from the 1:1 correlation are included in the trends. From the slopes of the trendlines, it is found that the concentrations of K <sup>+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup> , Ba <sup>2+</sup> and SO <sub>4</sub> <sup>2-</sup> are highest in DNS, whereas the concentrations of Na <sup>+</sup> and Sr <sup>2+</sup> are highest in OND.
The best correlation (within 5% difference) between OND and DNS is observed for Na <sup>+</sup> , $Ba^{2+}$ and $Mg^{2+}$ . In OND, these ions, but $Ba^{2+}$ , are also the ions with the most stable concentrations considering the standard deviations.
Large discrepancy in the Cl <sup>-</sup> concentrations is observed, which is especially visible in Figure 5; no trend is observed. Acid treatments (addition of HCl to the injected water) are applied to remove solid CaCO <sub>3</sub> forming in the wells. This introduces occasional sample events containing a high concentration of Cl <sup>-</sup> . These may cause the data points showing high Cl <sup>-</sup> concentrations observed at DHRTC ("Experimental" in Figure 4, and Y-axis in Figure 5.)
The best agreement between OND and DNS is, surprisingly, observed for Ba <sup>2+</sup> . Here, the slope of the fit is 1.0029, with a regression coefficient of R <sup>2</sup> =0.9517. However, for 9 of the 32 samples (28%), the Ba <sup>2+</sup> concentration is either not reported or reported as "0" in OND. Additionally, one of the remaining 23 points are excluded from the trend. The remaining points beyond the 25% deviation line are included in the trend. The missing Ba <sup>2+</sup> recordings may be explained as a missing measurement or it may be because the concentration is below the LOD (using IC). The samples with missing Ba <sup>2+</sup> concentrations in OND are also found to have the lowest Ba <sup>2+</sup> concentrations in DNS. Hence, this confirms the hypothesis that the Ba <sup>2+</sup> concentration in many of these samples most likely is below the LOD of the IC. This greatly underlines the importance of a more sensitive analytical technique (than IC) for the analysis of Ba <sup>2+</sup> in produced water as introduced with the use of ICP-OES.

 $\begin{array}{c}1\\2\\3\\4\\5\\6\\7\\8\\9\\10\\11\\12\\13\\14\\15\\16\\17\\18\\19\\20\\21\\22\\23\\24\\25\\26\\27\\28\\29\\30\end{array}$ 



Operator New Data calculated average concentration, mg/L Analyzed with IC (all ions)

Figure 5.

15
Ion	Linear trendline	Regression coefficient	Number of points		
	a x + b	R <sup>2</sup>	excluded in the trend		
Na <sup>+</sup>	0.9504 x + 464.78	0.7236	0		
K <sup>+</sup>	1.1933 x - 14.88	0.8365	5		
Mg <sup>2+</sup>	1.0455 x + 2.1904	0.9433	5		
Ca <sup>2+</sup>	1.2212 x - 216.25	0.8848	0		
Sr <sup>+</sup>	0.9168 x + 5.3133	0.9224	6		
Ba <sup>2+</sup>	1.0029  x + 0.9448	0.9517	1		
Cl-	No tren	d observed	-		
SO4 <sup>2-</sup>	1.1816 x - 78.405	0.9636	16		

Table 4.

### 3.3 Inter-instrumental test

Four of the cations; Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>, have also been analyzed with IC in the DHRTC New Samples. These were also analyzed using ICP-OES, which provides information for an inter-instrumental test. The sample set covers the total 61 DHRTC New Samples (DNS). The experimental results are given in Supplementary Material Table 10 and the parity plot comparing the results achieved with IC and ICP-OES, respectively, is given in Figure 6. The linear trendlines and their regressions coefficients are given in Table 5. The slope of the linear trendline is 1.0742, 0.9563, 0.943 and 0.7068 for Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>, respectively. Na<sup>+</sup> is the only ion that has been determined to have a higher concentration using IC; the remaining ions have lower concentrations determined with IC compared to ICP-OES.



### Figure 6.

The linear regressions are similar for K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>; here R<sup>2</sup> = 0.92 - 0.97. This is slightly better than for Na<sup>+</sup>, where R<sup>2</sup> = 0.82; but here, less points are also excluded from the trend. For all four cations, the concentrations determined are generally higher using the ICP-OES. This trend was also observed in the comparison between Operator New Data (OND) and DHRTC New Samples (DNS).

Elemental ion	Linear trendline a x + b	Regression coefficient R <sup>2</sup>	Number of points excluded in the trend
Na <sup>+</sup>	1.0742 x - 335.07	0.8178	2
K+	0.9563 x - 4.1115	0.9228	6
Mg <sup>2+</sup>	0.943 x - 9.2997	0.9672	7
Ca <sup>2+</sup>	0.7068 x + 156.3	0.9372	6

Table 5.

### 3.4 Inter-laboratory test

The Operator New Samples (71 samples in total) have been analyzed in two different laboratories (the operator's and DHRTC's). In the operator's laboratory, the samples were analyzed approximately one month after sampling. The determined compositions are given in OND. At DHRTC, these same samples were analyzed up to one year later, as the samples were not available any time sooner. In both laboratories, the analyses were carried out using IC. The compositions determined from the two analyses are compared in the parity plot displayed in Figure 7; the linear trendlines and regression coefficients are given in Table 6.

The linear trendlines for the cations have slopes ranging from 0.87 to 0.99; while Cl<sup>-</sup> displays notendand the tendobærved for  $SO_4^{2-}$  has a slope of 0.87 Allions have slopes lower than one, meaning that the concentration determined at DHRTC is lower than that determined by the operator. The best agreement is found for Na<sup>+</sup>, followed by K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+;</sup> these show good agreement between the two laboratories.  $SO_4^{2-}$  shows a poorer agreement (slope = 0.87) than the remaining ions (slopes > 0.96).

The good agreements observed for Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> suggest that the analysis of these is of high accuracy both in DHRTC's laboratory and in the operator's, thus, validating the (historical and new) data for these ions. Conversely, the Cl<sup>-</sup> plot appears very spread out, which questions the reliability of the measurement. As discussed in section 3.2, the Cl<sup>-</sup> concentrations may have been affected by acid treatments.

 $Sr^{2+}$  and  $Ba^{2+}$  are not included in this comparison as they have not been analyzed using IC at DHRTC.

Ion	Linear trendline	Regression coefficient	Number of points		
	a x + b	R <sup>2</sup>	excluded in the trend		
Na <sup>+</sup>	1.0947 x - 1130.1	0.7784	2		
K+	0.958 x + 16.98	0.9837	3		
Mg <sup>2+</sup>	0.9449 x + 10.119	0.9872	4		
Ca <sup>2+</sup>	0.9418 x - 33.009	0.9345	5		
Cl-	No tr	end observed	-		
SO4 <sup>2-</sup>	0.8682 x + 69.416	0.9829	16		

#### Table 6.

One thing to note here is that the concentrations measured at DHRTC are measured up to one year later than the samples were collected; and the concentrations measured at the operator were measured within one months after the samples were collected. This change in time may itself change the composition of the samples. A study of this is presented in a publication in draft by the authors of this publication.



Analyzed with IC

2

Figure 7.

### 4 Discussion

### 4.1 Guidelines for future analyses

From the experience gained from the presented study, some guidelines for future analysis are given forward. These may be useful for produced water samples, but also similar samples (water samples with high salinity matrix, potentially containing organic residues and micro bacteria).

- The samples must be filtered prior to analysis to avoid contamination from suspended solids. This is especially relevant for ICP-based techniques.
- For a sensitive determination of Ba<sup>2+</sup>, ICP-OES is advised. This is found important for an accurate prediction of the scale formation risk.
- For the ICP-based analyses a NaCl matrix is needed in the calibration standards.
- The use of hydrochloric acid for sample preservation should be avoided if chlorine concentrations are of interest.

### 4.2 Prediction of scale formation risk

In many of the oil fields in the Danish North Sea, including the Halfdan field, scale has proven to be a significant risk, which will affect field producibility, lifetime and, consequently, field economics. [22] Some of these scales include the hard insoluble BaSO<sub>4</sub> and SrSO<sub>4</sub> scales. Also, CaCO<sub>3</sub> has been identified. [27, 12, 13, 14, 15] SrSO<sub>4</sub> and BaSO<sub>4</sub> are mainly critical when formed in the wellbore area. [22] The prediction of scale formation is complicated, and still, the most widely used indicator of the scale potential is the ionic compositions of the produced water. The Halfdan field is one of the fields in the Danish North Sea that is especially sensitive to scale formation because it is extensively water flooded and the injection water introduces large amounts of SO<sub>4</sub><sup>2-</sup>. Figure 2 shows a map of Halfdan with the w<u>g</u>lls where scale has been observed pointed out. The information on observed scale is based on measurements of the inner diameter of the specific wells and is received from the field operator.

The ionic composition of nine samples have been subject to scale prediction calculations using the Extended UNIQUAC model. These were chosen to represent the extremes in the total sample set: 1) High Ba<sup>2+</sup> (>2 mg/L) combined with high SO<sub>4</sub><sup>2-</sup> (>450 mg/L), 2) extremely high Ba<sup>2+</sup> (>30 mg/L), 3) high Sr<sup>2+</sup> (≈150 mg/L) combined with high SO<sub>4</sub><sup>2-</sup> (>500 mg/L), 4) extremely high SO<sub>4</sub><sup>2-</sup> (>1000 mg/L), and 5) low Ba<sup>2+</sup> (<0.8 mg/L) combined with low SO<sub>4</sub><sup>2-</sup> (<200 mg/L). For all but 4), two samples are included. For 4) one sample is included in the calculation.

It is important to note that the output only gives an indication of the potential risk for solid formation. Most likely, the system never reaches equilibrium because the conditions change rapidly. Also, kinetics and other factors playan important role in scale formation. The calculated saturation indices (SI) and the potentially formed solid (mg/L) at equilibrium for the nine samples are given in Supplementary

Material Table 11. This shows that samples 9, 12, 13 and 30, at all conditions, are supersaturated with respect to CaCO<sub>3</sub>. Interestingly, these also all show to be supersaturated with respect to BaSO<sub>4</sub>. These four samples are from extreme categories 1), 3) and 5) in the list above. That is, no correlation with them all having eg. high SO42- is identified. Considering CaSO4, all samples are undersaturated independently of the conditions (SI =  $5 \cdot 10^{-3} - 3 \cdot 10^{-2}$ ). More critically is BaSO<sub>4</sub>: All samples are supersaturated at all conditions; but samples number 13 and 30, which are only supersaturated at ambient and cool storage conditions. Not surprisingly, these are both from extreme category 5), which are the samples with low Ba<sup>2+</sup> combined with low SO<sub>4</sub><sup>2-</sup>. At ambient conditions, the expected solid concentrations range from 0.1 mg/L to 6 mg/L in the low Ba<sup>2+</sup> samples. For the two samples with high Ba<sup>2+</sup>, the expected solid concentration exceeds 50 mg/L. These levels are significant and may cause precipitation of scales. Also, they highlight the importance of a sensitive analysis of Ba<sup>2+</sup> even when the levels in the produced water are significantly below 1 mg/L. SrSO<sub>4</sub> is found to be supersaturated only in the samples with an extremely high SO42- content (>1000 mg/L). The expected solid concentrations are similar for all conditions and are determined to be approximately 190 mg/L. The wells where the calculations presented here predict that scale may cause problems are marked in Figure 2. Based on the presented calculations, all included wells are predicted to form scale also, HDA-6, where scale explicitly has not been observed. It is clearly shown from Figure 2 that scale is a severe problem across the entire Halfdan field.

Calculations based on water chemistry is a strong tool for the prediction as it is much easier, faster and cheaper than the physical measurements.

The expected concentrations of both  $BaSO_4$  and  $SrSO_4$  are found to be higher at ambient and cool storage conditions than at reservoir conditions. These scales are especially critical when formed in the deeper wells, which is at reservoir conditions, as these are impossible to reach with cleaning tools. All the tested samples are from different wells, and collected between October 2018 and February 2019. The fact that the samples are fairly recent and distributed on the entire field suggests that the operator must be highly aware of this risk of formation of both  $SrSO_4$  and  $BaSO_4$ that may be present at current times. This risk increases with the increased level of  $SO_4^{2-}$  that is a common consequence of water injection. [6]

### 5 Concluding remarks

Good agreement between reported data (Operator New Data) and results from analysis of new samples (DHRTC New Samples) for Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>and SO<sub>4</sub><sup>2-</sup> is observed. The linear trendlines have slopes between 0.92 and 1.19. This validates the analysis of DHRTC New Samples as well as the received data for these ions. Cl<sup>-</sup> display no clear trend but the levels are as expected, which is approximately 20 000 to 40 000 mg/L.

An inter-instrumental study of the concentrations of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> shows an agreement between IC and ICP-OES with trendline slopes of 0.71 to 1.07, which is satisfactory. The best agreement is observed for Na<sup>+</sup> and the poorest for Ca<sup>2+</sup>.

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1 2 3 An inter-laboratory test shows good agreement between laboratories for the 4 analysis of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>; slopes are above 0.87. Again, Cl<sup>-</sup> shows 5 no trend. Sr<sup>2+</sup> and Ba<sup>2+</sup> was not included in this test. 6 7 Most of the samples show significant potential for scale formation, which 8 underlines the importance of keeping track of the chemical composition of the 9 produced water. Especially, the insoluble scales BaSO4 and SrSO4 may affect field 10 production and economy. Thus, a sensitive analysis of  $Ba^{2+}$  and  $Sr^{2+}$  (and  $SO_4^{2-}$ ) is 11 crucial. The real novelty of the work presented here is in the ability to analyze Ba<sup>2+</sup> 12 at naturally present levels, which has not been possible with the previously used 13 methods (IC and titration). The introduction of ICP-OES lowers the LOD 14 significantly and allows for a more rapid analysis which also includes the analysis of  $\frac{15}{16}$  $Ba^{2+}$  (and other cations if relevant) at levels below 1 mg/L. 17 18 Acknowledgements 19 20 Weacknowledge TOTAL for providing the production data and produced water 21 samples and the Danish Underground Consortium (TOTAL, Noreco and 22 Nordsøfonden) for granting permission to publish this work. This work was 23 economical supported by the Danish Hydrocarbon Research and Technology Centre 24 (DHRTC). Charlotte Lassen (DHRTC) is thanked for support with retrieving data, 25 samples and establish contact to specialists from TOTAL. Annette Eva Jensen has 26 been a priceless support in the laboratory, assisting with the sample preparation and 27 analysis. A sincere thanks goes to Dr. Sharath Mahavadi for reading the article 28 through and provide valuable feedback on the manuscript. 29 Conflict of interest statement 30 31 No conflicting interests to report. 32 33 References 34 35 [1] Danish Energy Agency. "Oil and Gas Production in Denmark" available at 36 "https://ens.dk/sites/ens.dk/files/OlieGas/oil\_and\_gas\_in\_denmark\_2013.pdf". 37 2013. 38 [2] M. Abdou, A. Carnegie, S. G. Mathews, K. McCarthy, M. O'Keefe, B. 39 Raghuraman, W. Wei, and C.G. Xian. "Finding Value in Formation Water". 40 Oilfield Review Spring, 23(1):p. 24-35, 2011. 41 [3] S. J. Houston, B. Yardley, P.C. Smalley, and I. Collins. "Precipitation and 42 Dissolution of Minerals During Waterflooding of a North Sea Oil Field" 43 (SPE100508). SPE International Oilfield Scale Symposium, pages p. 1-6, 2006. 44 45

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10	
11	Figure captions
12	
13	Figure 1: Visualisation of the presented study.
14 15 16 17	<b>Figure 2:</b> Map of the Halfdan field. From Danish Energy Agency. [1] Information on scale observations and predictions has been added by the authors. The information is based on observations reported by the field operator (observations) combined with results found in the work presented here (predictions).
18 19	<b>Figure 3:</b> Selection of data points (OND) to match physical water sample (DNS).
20 21 22 23 24	<b>Figure 4:</b> Comparison of results from experimental analysis of DHRTC New Samples (DNS) and the calculated average of corresponding samples in Operator New Data (same well, within a two week interval). The average of OND (point) is given with the standard deviation included (black error bars). See the text for further details.
25 26 27 28 29 30 31	<b>Figure 5:</b> Parity plots illustrating the trend between the average of the reported concentrations in Operator New Data (OND) and the measured value from DHRTC New Samples (DNS). The OND concentrations are measured using IC, and the DNS concentrations using a combination of ICP-OES (for the cations) and IC (for the anions). The solid lines represents the 25% deviation from a one-to-one correlation, which is marked by the dotted line.
32 33	<b>Figure 6:</b> Inter-instrumental test (IC vs. ICP-OES): Parity plots. The solid lines represents the 25% deviation from a one-to-one correlation, which is marked by the dotted line.
34 35 36 37 38	<b>Figure 7:</b> Inter-laboratory test (DHRTC vs. operator (all IC): Parity plots. The solid lines represents the 25% deviation from a one-to-one correlation, which is marked by the dotted line.
40	Table 2: Summary of produced water samples.
41 42 43	<b>Table 2:</b> The average composition of produced water and the analytical technique(s) used.
44 45	<b>Table 3:</b> The selected mode and analytical wavelengths used for the mentioned ions in the analysis of produced water using ICP-OES.

1 2 3	<b>Table 4:</b> Comparison of experimental measurements of DHRTC New Samples (DNS) with the calculated average from Operator New Data (OND): Linear trendline equations and their regression coefficients for the parity plots shown in Figure 5.
4	
5	Table 5: Inter-instrumental test (IC vs. ICP-OES): Linear trendline equations and their
6	regression coefficients for the parity plots shown in Figure 6.
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8	<b>Table 6:</b> Inter-laboratory test (DHRTC vs. operator (all IC): Linear trendline equations and their
9	regression coefficients for the parity plots shown in Figure 7.
10	
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12	Addreviations
13	
14	DHRIC = Danish Hydrocarbon Research and Technology Center
15	DNS = DHRIC New Samples
16	NC = North Central
17	NE = North East
18	NW = North West
19	OND = Operator New Data
20	ONS = Operator New Samples
21	ICP-OES = Inductively coupled plasma – optical emission spectroscopy
22	PWC = Produced water chemistry
23	SE = South East
24	SW = South West
25	
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27	Estimated length: 9 pages
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1										
2	Supplementary Material									
3										
4	Produced water from the North Sea									
5	- A case study and analytical guidelines									
6 7	Sofie N. Bergfors, Simon I. Andersen, Karen L. Feilberg									
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10	1 Experimental details									
11 12 13	<b>1.1</b> Sample preparation: Dilution factors									
10	Technique Dilution factor									
	ICP-OES 70									
	IC, cations 100									
14	Table 1: Sample dilution factors.									
15 16										
10	1.2. ICP-OFS: Plasma narameters									
18										
19	Parameter Value									
	Plasma Stabilization Time 10 min									
	Flush Pump Rate 50 rpm									
	Analysis Pump Rate 50 rpm									
	RF Power 1150 W									

Nebulizer Gas Flow Coolant Gas Flow Auxiliary Gas Flow

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 Table 2:
 Plasma parameters.

0.6 L/min 12 L/min 1.0 L/min

### **1.3 ICP-OES: Calibration standards**

		Сс	Calibration			
Elen	nent C	1 C2	C3	C4	Stock	Regression
Bulk ions						
Na <sup>+</sup>	60	) 150	300	600	3000	0.958 - 0.995
K+	2	5	10	20	100	0.958 – 1
Mg <sup>2</sup>	+ 1.	4 3.5	7	14	70	0.959 – 1
Ca <sup>2+</sup>	0.	2 0.5	1	2	10	0.902 - 0.999
Trace ions						
Na <sup>+</sup>	90	) 180	450	900	9000	Not analyzed
Sr <sup>2+</sup>	0.	51	2.5	5	50	0.999 - 1
Ba <sup>2+</sup>	0.0	05 0.01	0.025	0.05	0.5	0.996 - 0.999

**Table 3**: Composition of calibration solutions for the bulk element and trace element analysis using ICP-OES. C1-C4 are used for the calibration of the instrument and are prepared from a dilution of the stock solution.

### 1.4 ICP-OES: Performance control and sequencing

At the start of every day, a reference standard with 2 mg/L Zn is run as a control for the daily performance. The minimum axial and radial intensity is 1800 and 20000 counts per second (cps), respectively. If these criteria are not met, analyses are not to be run.

All analyses are started with a series of calibration standards including a blank (2% nitric acid). The sequence is followed by nine samples and one QC followed by a wash containing 2% nitric acid, and repeated until all samples have been analyzed. A blank (2% nitric acid) is randomly run at every 20-30 samples to check for carry over. Before shut down, a wash of 4% nitric acid, followed by 2% nitric acid is run to rinse the tubing.

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### **1.5 IC: Calibration standards**

		(	Concentrat	Calibration		
	Element	C1 C2		C3	C4	regression
Anions						
	Cl-	40	60	80	100	0.9932 - 0.9981
	SO42-	1	2	5	10	0.9976 - 1
Cations						
	Na+	88.2	114.2	137.2	-	0.9526 - 0.999
	Ca <sup>2+</sup>	1.1	5.7	11.5	-	0.9996 – 1
	Mg <sup>2+</sup>	11.1	17.3	23.0	-	0.9867 - 1
	K+	2.3	4.6	6.9	-	0.9996 - 1

3 4 **Table 4**: Composition of calibration standards (C1-C4) for the analysis of anions and cations using IC.

### 2 Results

### 2.1 Experimentally determined compositions of DHRTC New Samples

**Table 5**: Compositions of DHRTC New Samples determined with ICP-OES (cations) combined with IC (anions). All samples have been collected at the Halfdan Field: SE = South East, NW = North West, NC = North Central, SW = South West. The concentrations are given in mg/L "nd" = "not detected".

### 2.2 Sample composition from Operator New Data

Sample number		Samples	les Concentration mg/I							
and location		included	NIa+	<b>V</b> +	M~2+		1011, 111§	2/L Pa <sup>2+</sup>	$C_{1}$	SO 2-
1	A	menuueu	17072	105	Mg <sup>2</sup> '	Ca21	5r <sup>2</sup> '	Da <sup>2</sup>	20205	5042
	Averag		17973	135	266	952	140	0.0	30285	545
SE	Deferre	2	165	0	0	20	10.5	0.0	390	62
	Defore	3								
_	After	3	10/1/							100
2	Averag		18616	136	259	972	143	0.3	31371	439
SE	Std.dev.		892	11	10	40	16.0	0.4	1584	219
	Before	3								
	After	3								
3	Averag		16685	151	327	890	131	0.8	28366	678
SE	Std.dev.		348	14	45	49	10.7	1.3	524	161
	Before	3								
	After	3								
4	Averag		16737	147	331	891	130	0.0	28204	682
SE	Std.dev.		105	6	8	46	6.3	0.0	119	15
	Before	3								
	After	3								
5	Averag		15761	88	207	1055	107	28.6	27118	57
??	Std.dev.		5838	31	75	377	37.9	11.1	10084	39
	Before	2								
	After	3								
6	Averag		16200	121	297	788	92	3.7	27488	163
NC	Std.dev.		220	8	9	36	6.6	2.6	264	13
	Before	3								
	After	3								
7	Averag		17402	129	240	958	153	0.5	28972	342
SE	Std.dev.		169	1	1	24	3.0	0.9	230	8
	Before	1								
	After	3								

**Table 6:** The calculated average composition (average) and the standard deviation (std.dev) given in mg/L. The number of samples included in the calculation is also given. The calculations are based on Operator New Data. Samples 1-12.

Sample number		Samples			Со	ncentra	tion, mg	g/L		
and location		included	Na+	K+	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>	Cl-	SO42-
8	Averag		16552	143	334	876	129	0.8	28271	607
SE	Std.dev.	_	1295	45	200	94	31.3	0.9	1913	463
	Before	3								
	After	3								
9	Averag		16537	139	335	840	125	0.8	28114	586
SE	Std.dev.	-	1282	46	200	82	29.2	0.9	1842	465
	Before	3								
	After	3								
10	Averag		16837	147	348	860	108	0.8	28630	436
NC	Std.dev.	-	1173	9	41	66	27.8	1.3	2000	99
	Before	2								
	After	3								
11	Averag		16650	145	351	847	108	0.8	28456	446
NC	Std.dev.	-	1145	7	38	69	25.5	1.2	1914	89
	Before	3								
	After	3								
12	Averag		16055	147	373	811	102	1.3	27559	452
NC	Std.dev.	-	228	2	6	35	5.1	1.1	647	28
	Before	3								
	After	3								
13	Averag		13076	273	862	739	41	3.3	23155	1688
NC	Std.dev.		1395	104	376	310	35.1	5.6	2154	950
	Before	1								
	After	3								
14	Averag		12749	290	941	675	35	2.6	22663	1927
NC	Std.dev.	-	1231	101	411	289	50.2	5.5	2898	1005
	Before	3								
	After	3								
15	Averag		15136	185	530	739	66	1.0	25732	662
NC	Std.dev.		1088	34	168	104	46.8	0.0	1655	238
	After	3								
16	Averag		15006	179	559	726	71	0.0	26088	719
NC	Std.dev.		241	8	20	31	2.9	0.0	373	31

**Table 7:** The calculated average composition (average) and the standard deviation (std.dev) given in mg/L. The number of samples included in the calculation is also given. The calculations are based on Operator New Data. Samples 8-16.

Sample number		Samples			Со	ncentra	tion, mg	g/L		
and location		included	Na+	K+	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>	Cl-	SO42-
17	Average		14825	178	551	688	67	1.5	25533	742
NC	Std.dev.		87	5	15	17	1.2	1.1	232	43
	Before	3								
	After	3								
18	Average		18875	131	238	966	142	0.0	31588	479
??	Std.dev.		190	10	6	31	13.8	0.0	511	38
	Before	3								
	After	3								
19	Average		18855	132	240	964	150	0.0	31731	513
??	Std.dev.		212	3	6	45	5.3	0.0	569	18
	Before	3								
	After	1								
20	Average		16733	109	251	920	110	3.0	28318	82
SE	Std.dev.		242	4	10	24	9.3	2.5	570	18
	Before	2								
	After	3								
21+22	Average		16763	106	232	844	70	9.7	28022	18
NE	Std.dev.		290	11	8	34	12.2	1.3	436	5
	Before	1								
	After	3								
23	Average		16837	103	235	865	82	7.6	28552	19
NE	Std.dev.		215	10	8	42	18.5	3.9	647	4
	Before	3								
	After	3								
24	Average		15938	106	275	2275	97	15.3	29661	72
NE	Std.dev.		375	7	18	752	1.1	3.5	1247	36
	Before	3								
	After	3								

**Table 8**: The calculated average composition (average) and the standard deviation (std.dev.) given in mg/L. The number of samples included in the calculation is also given. The calculations are based on Operator New Data. Samples 17-24.

Sample number		Samples			Co	ncentra	tion, my	g/L		
and location		included	Na+	$K^+$	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>	Cl-	SO42-
25	Average		17450	197	377	804	119	0.0	29079	907
NW	Std.dev.		63	4	6	20	1.0	0.0	421	29
	Before	1								
	After	3								
26+27	Average		17423	192	376	802	117	0.2	29044	911
NW	Std.dev.		77	11	6	19	4.1	0.4	383	28
	Before	2								
	After	3								
28	Average		22310	295	305	1215	62	0.4	82381	760
NW	Std.dev.		58	1	3	30	3.9	0.0	566	0
	Before	0								
	After	3								
29	Average		21992	207	244	960	132	0.0	36245	749
NW	Std.dev.		164	5	3	49	5.4	0.0	418	11
	Before	3								
	After	3								
30	Average		23704	217	309	1090	155	0.0	39440	867
SW	Std.dev.		236	1	4	37	7.3	0.0	582	25
	Before	2								
	After	3								
31	Average		17955	221	467	905	115	0.5	30325	1136
SW	Std.dev.		858	23	46	17	5.6	0.9	1890	338
	Before	1								
	After	3								
32	Average		19341	221	452	946	127	0.3	32309	1137
SW	Std.dev.		3095	18	74	61	15.0	0.8	4941	309
	Before	3								
	After	3								

**Table 9:** The calculated average composition (average) and the standard deviation (std.dev.) given in mg/L. The number of samples included in the calculation is also given. The calculations are based on Operator New Data. Samples 25-32.

	Con	centra	tion in m	ng/L	(	Difference in %				
XA7 11 1	-	Т	IC 2+	2+	(ICI	P-OES -	IC) / ICI	2-OES		
Well location	Na⊤	Кт	Mg∠+	Ca∠+	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>		
NC	15821	197	427	657	5%	-10%	13%	8%		
NC	16912	160	348	713	-22%	2%	3%	8%		
NC	16740	160	368	689	-4%	-54%	-80%	23%		
NC	17549	156	303	682	1%	-8%	18%	5%		
NC	12895	327	979	341	-7%	6%	15%	35%		
NC	12913	335	1046	518	-5%	-2%	-4%	8%		
NC	15388	146	525	365	-9%	37%	24%	43%		
NC	nd	199	574	591	nd	5%	6%	13%		
NC	13621	137	262	526	11%	18%	49%	7%		
NC	14997	129	331	734	2%	-25%	-35%	53%		
NC	nd	16	110	1091	nd	86%	63%	-46%		
NC	16891	83	156	635	-1%	41%	39%	28%		
NC	13533	97	135	825	25%	-12%	29%	3%		
NC	16235	135	314	664	-1%	6%	2%	13%		
NE	16463	109	226	765	10%	23%	23%	30%		
NE	16670	115	271	1290	-7%	30%	29%	-67%		
NE	15603	111	244	794	3%	5%	6%	18%		
NE	16973	122	265	836	-5%	-1%	-1%	14%		
NE	17167	114	228	759	8%	24%	22%	29%		
NE	15798	112	264	1980	6%	19%	18%	21%		
NE	nd	7	51	986	nd	93%	77%	-43%		
NW	14061	274	743	588	11%	-5%	-11%	28%		
NW	nd	202	332	799	nd	20%	15%	31%		
NW	17876	nd	nd	nd	5%	nd	nd	nd		
NW	nd	119	115	723	nd	29%	62%	-4%		
NW	16776	238	545	687	-14%	2%	-5%	6%		
NW	nd	130	143	709	nd	33%	62%	8%		
NW	24955	215	237	892	-12%	27%	22%	27%		
	Table continues on next page									

### 2.3 Inter-instrumental test: IC and ICP-OES

	Con	Concentration in mg/L			Difference in %			
Well location	Na <sup>+</sup>	к+	Mg <sup>2+</sup>	Ca <sup>2+</sup>	(IC Na	-P-OES + κ <sup>+</sup>	$M_{\sigma}^{2+}$	$C_{2}^{2+}$
NW	23200	209	218	842	-5%	-5%	12%	<u>4%</u>
NW	14635	235	568	731	3%	11%	12%	18%
SE	18330	147	229	868	4%	22%	20%	24%
SE	nd	44	54	1144	nd	66%	76%	-46%
SE	18194	150	259	893	-12%	5%	-3%	5%
SE	19334	161	257	901	-15%	8%	2%	6%
SE	15264	103	252	1433	-2%	30%	33%	-52%
SE	18853	167	333	734	-10%	10%	11%	24%
SE	14722	94	207	796	4%	10%	10%	20%
SE	15163	96	199	829	-1%	2%	2%	13%
SE	17464	120	217	626	-7%	16%	13%	28%
SE	18220	138	265	800	-34%	53%	71%	-24%
SE	13591	127	157	757	29%	-6%	36%	8%
SE	14311	274	841	546	9%	-123%	-194%	61%
SE	14126	261	738	535	11%	-8%	12%	10%
SE	16945	123	239	802	-11%	6%	2%	7%
SW	24470	211	323	878	-17%	24%	20%	30%
SW	16011	208	299	939	28%	-8%	10%	1%
SW	24085	218	296	1031	-12%	21%	18%	19%
SW	22466	251	513	867	-16%	9%	8%	20%
SW	20911	237	496	866	-6%	-12%	2%	1%
SW	nd	245	315	1061	nd	23%	16%	26%
SW	16978	166	95	1094	19%	17%	65%	-19%
SW	16076	237	265	1032	35%	27%	21%	28%
SW	26775	212	82	1487	-19%	-2%	68%	-59%
SW	nd	157	376	788	nd	32%	72%	26%
SW	16287	186	369	786	-7%	5%	-3%	7%
SW	18867	219	506	758	-8%	-25%	2%	5%
SW	15490	229	521	781	5%	11%	18%	14%
SW	17912	272	748	574	4%	-38%	2%	28%
Absolute					9%	14%	18%	18%
average								
deviation								

 **Table 10**: Concentrations determined with IC in mg/L and the comparison to the concentration determined using ICP-OES, with the difference given in %. "nd" = "not detected".

### 2.4 Thermodynamic modelling

		Reservoir		Ambient		Cool storage	
Sam	nple number	SI	(s), $mg/L$	SI	(s), $mg/L$	SI	(s), mg/L
10	ip ie indine ei		(0), 116, 2	01	(0), 116, 2	01	(5)/ 116/ 2
12	6-60	1 11 10-6	0.0	1 1 5 10-5	0.0	0 00 10-5	0.0
	$SrSO_4$	1.41×10 °	0.0	1.15×10 <sup>-5</sup>	0.0	2.39×10 <sup>-5</sup>	0.0
	BaSO <sub>4</sub>	1.00	5.0	1.00	5.8	1.00	5.9
	CaCO <sub>3</sub>	1.00	654.1	1.00	227.9	1.00	227.5
	CaSO <sub>4</sub>	$2.01 \times 10^{-2}$	0.0	$1.63 \times 10^{-2}$	0.0	$1.25 \times 10^{-2}$	0.0
16							
	$SrSO_4$	$6.73 \times 10^{-1}$	0.0	$6.30 \times 10^{-1}$	0.0	$6.06 \times 10^{-1}$	0.0
	$BaSO_4$	1.00	4.4	1.00	5.5	1.00	5.6
	$CaCO_3$	$1.10 \times 10^{-11}$	0.0	$1.02 \times 10^{-12}$	0.0	$4.53 \times 10^{-13}$	0.0
	CaSO <sub>4</sub>	$2.93 \times 10^{-2}$	0.0	$2.43 \times 10^{-2}$	0.0	$2.00 \times 10^{-2}$	0.0
5	-		010		0.0		0.0
Ũ	SrSO	$2.13 \times 10^{-1}$	0.0	$1.70 \times 10^{-1}$	0.0	$1.55 \times 10^{-1}$	0.0
	BaSO.	2.15×10	0.0 40 1	1.70×10	0.0 E1 0	1.00 × 10	0.0 E1 E
		1.00	40.1	1.00	51.2	1.00	51.5
	$CaCO_3$	1.16×10 <sup>10</sup>	0.0	1.01 × 10 ···	0.0	4.51×10 ···	0.0
	$CaSO_4$	$1.42 \times 10^{-2}$	0.0	$1.01 \times 10^{-2}$	0.0	$8.09 \times 10^{-5}$	0.0
11							
	$SrSO_4$	$5.65 \times 10^{-1}$	0.0	$4.51 \times 10^{-1}$	0.0	$4.13 \times 10^{-1}$	0.0
	$BaSO_4$	1.00	50.9	1.00	52.1	1.00	52.3
	$CaCO_3$	$9.05 \times 10^{-11}$	0.0	$7.86 \times 10^{-12}$	0.0	$3.51 \times 10^{-12}$	0.0
	CaSO <sub>4</sub>	$3.20 \times 10^{-2}$	0.0	$2.31 \times 10^{-2}$	0.0	$1.84 \times 10^{-2}$	0.0
9							
	SrSO₄	$1.39 \times 10^{-6}$	0.0	1 14 ×10 <sup>-5</sup>	0.0	$2.36 \times 10^{-5}$	0.0
	BaSO4	1.00	0.0	1.11/10	3.0	1.00	3.0
	$C_{2}C_{2}$	1.00	2.2 (E4 2	1.0	228.0	1.00	3.0 227 7
		1.00	654.5	1.0	228.0	1.00	227.7
10	$CaSO_4$	2.61×10 <sup>2</sup>	0.0	2.04×10 <sup>-2</sup>	0.0	1.56×10 <sup>-2</sup>	0.0
19	6.60	a <b>-</b> a - ta - 1		<b>-</b> aa ta-1		1	
	$SrSO_4$	$8.50 \times 10^{-1}$	0.0	$5.88 \times 10^{-1}$	0.0	$5.25 \times 10^{-1}$	0.0
	$BaSO_4$	1.00	0.6	1.00	1.6	1.00	1.7
	CaCO <sub>3</sub>	$4.89 \times 10^{-10}$	0.0	$3.60 \times 10^{-11}$	0.0	$1.61 \times 10^{-11}$	0.0
	CaSO <sub>4</sub>	$3.19 \times 10^{-2}$	0.0	$2.09 \times 10^{-2}$	0.0	$1.64 \times 10^{-2}$	0.0
10							
	SrSO <sub>4</sub>	1.00	185.5	1.00	186.3	1.00	186.6
	BaSO₄	1.00	34	1.00	47	1.00	49
	$CaCO_2$	$3.02 \times 10^{-13}$	0.0	$3.14 \times 10^{-14}$	0.0	$1.42 \times 10^{-14}$	0.0
	CaSO4	$3.80 \times 10^{-2}$	0.0	$3.73 \times 10^{-2}$	0.0	$3.22 \times 10^{-2}$	0.0
12	Ca5O4	5.09×10	0.0	5.75×10	0.0	5.25×10	0.0
13	S#60	6.00 - 10-2	0.0	$4.70 \times 10^{-2}$	0.0	4 4E × 10-2	0.0
	5r504	6.89×10 <sup>-2</sup>	0.0	4.70×10 -	0.0	4.45×10 <sup>2</sup>	0.0
	ва504	$5.28 \times 10^{-1}$	0.0	1.00	0.7	1.00	0.9
	CaCO <sub>3</sub>	1.00	615.9	1.00	225.7	1.00	226.5
	CaSO <sub>4</sub>	$6.43 \times 10^{-3}$	0.0	$5.78 \times 10^{-3}$	0.0	$4.59 \times 10^{-3}$	0.0
30							
	$SrSO_4$	$2.70 \times 10^{-8}$	0.0	$2.34 \times 10^{-7}$	0.0	$4.49 \times 10^{-7}$	0.0
	$BaSO_4$	$2.85 \times 10^{-1}$	0.0	1.00	0.1	1.00	0.5
	CaCO <sub>3</sub>	1.00	650.2	1.00	226.4	1.00	226.4
	CaSO <sub>4</sub>	$1.66 \times 10^{-3}$	0.0	$2.23 \times 10^{-3}$	0.0	$2.01 \times 10^{-3}$	0.0

**Table 11**: Calculated saturation index (SI) and solid formation (s) for nine selected samples. The SI is unit less and the solid formed is given in mg/L. The calculation have been carried out using ScaleCERE.

### A.3 Paper 3 Produced water from the North Sea – A case study and analytical guidelines. Part 2: Impact of storage

Contributions: Sofie N. Bergfors framed the study and developed the analytical workflow. Annette E. Jensen and Sofie N. Bergfors carried out the experimental work related to sample preparation and analysis. Sofie N. Bergfors analyzed the data and wrote the manuscript under the supervision of Simon I. Andersen and Karen L. Feilberg. All authors performed scientific and grammatical revisions of the final draft.

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## Produced water from the North Sea A case study and analytical guidelines Part 2: Impact of storage

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#### Abstract

Water is co-produced with oil from oil producing wells. The produced water is routinely analyzed as its ionic composition (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) is used to follow injection water breakthrough, monitor the well performance and track potential scale precipitation and corrosion in the wells. Samples are often stored in case of need for later analysis; for example if new questions are to be answered or because new analytical techniques have made new measurements possible, allowing additional information to be extracted from the produced water. The study presented here employs a recently developed new analytical workflow for the analysis of produced water samples to evaluate the potential changes in the sample composition, which may occur during storage (one year). Contrary to general assumptions, no significant changes in the sample composition with respect to the major ions were observed after one year, suggesting that stored samples maintain most of their analytical value.

**Keywords:** Produced water chemistry (PWC), long-time storage, water analysis, Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Ion Chromatography (IC)

### 1 Introduction

The ionic composition of produced water (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) from oil production wells is routinely analyzed in order to monitor the well performance and track potential scale precipitation and corrosion in the wells. [1, 2] The most harmful scales, including the hard insoluble scales SrSO<sub>4</sub> and BaSO<sub>4</sub>, are an operational risk and very costly to remove. In the worst case, they may cause shut down of parts of the producing wells. The potential formation of scales is dependent on the concentrations of some of the major ions in the flowing water. Therefore, a reliable monitoring of the chemical composition of the produced water is of great interest for the oil producing companies. This interest applies especially for companies operating in North Sea Chalk, which is composed of clay sized carbonate grains. The carbonate rock is potentially chemically and physically reactive during production. [3, 4, 5, 6] Furthermore, the produced water composition informs the choice of enhanced oil recovery (EOR) strategies, production management materials, and water handling strategy. [7]

From the time of production to the point of analysis, the produced water samples are exposed to significant physical changes. Especially, the pressure and temperature changes are significant. In the reservoir these are approximately 17000 kPa and 70°C, respectively (the Halfdan field use as case). [8] At the surface - ambient conditions - the pressure and temperature is approximately 100 kPa and 20°C, respectively. The concentrations of HCO3 changes from approximately 400 mg/L in the reservoir to 140 mg/L at the surface. [9] These changes affect the thermodynamic equilibrium in the samples significantly, and consequently, the chemical composition of the samples. [10] Most often, produced water samples, produced off-shore in the Danish North Sea, are analyzed on-shore within 2-4 weeks after sampling. At this point in time, the ionic composition of the samples may have changed due to equilibration with the ambient conditions (CO<sub>2</sub>) and, thus, does not fully represent the composition of the water present in the reservoir. To avoid this, it is advantageous to analyze the samples at the platforms, preferably in flow at the production point. Practically, this is almost impossible. The expected changes from reservoir to analysis points are estimated using thermodynamic modelling. In the presented work, the ScaleCERE program, based on the Extended UNIQUAC model is used for this purpose. The thermodynamic calculations are briefly discussed in the present work and presented in full in a previous work: "Bergfors et al., 2020". [11]

Due to the great relevance of the produced water chemistry (PWC), samples are often re-analyzed to answer new questions or because new techniques have become available. In many laboratories, produced water (PW) samples are stored for a number year in case of need. Commonly, PW samples are stored cooled, in the dark to limit the changes in the sample compositions during storage. Again, the physical conditions of the sample is changed slightly – the temperature is changed from ambient temperature around 20°C to colder conditions around 5°C.

Reliable and presentative analytical results require that the samples are representative and that the compositions of them have not changed significantly. Whether the sample composition remains unchanged during storage or not has, to our knowledge, never been studied in depth and reported in the open literature for a large set of samples. Some of the known potential changes include salt formation of chlorides (MgCl<sub>2</sub>, CaCl<sub>2</sub>, NaCl) and sulphate salts (SrSO<sub>4</sub> and BaSO<sub>4</sub>). From predictive calculations presented in previous work, it was found that some samples are supersaturated with respect to CaCO<sub>3</sub>, BaSO<sub>4</sub> and/or SrSO<sub>4</sub> at ambient and cool storage conditions. [9, 11] Additionally, it is known that microbiological activity may deplete SO<sub>4</sub><sup>2-</sup> (sulphate reducing bacteria) to form H<sub>2</sub>S. [14, 15, 16] To limit this effect, samples are normally preserved through the addition of HCl and/or HNO<sub>3</sub>.

A previous publication ("Bergfors *et al.*, 2020") presents a new analytical workflow for the sample preparation and analysis of produced water samples from the Danish North Sea. [11] This method utilizes the high-sensitivity of Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) combined with its ability for multi-elemental analysis. The presented method using ICP-OES covers the ions Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup>. For the analysis of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, Ion Chromatography (IC) is used. The achieved analytical results were compared with data on similar samples from the operator. Furthermore, an inter-laboratory and inter-instrumental study is presented. This all feed into the evaluation of the new analytical workflow – and the quality of the existing (historical) data on the samples composition. Fortunately, good agreement and reproducibly were observed; thus, validating the new analytical workflow and the historical data. [11]

The presented study aims to evaluate on the observed changes in the produced water chemistry (PWC). Samples from the Danish Halfdan field are included as a case study and the analytical workflow presented in "Bergfors *et al.*, 2020" is applied throughout the work. [11]

To bring the reported compositions into perspective, recently classified water types are included. We have recently classified two different produced water types, both produced at the Halfdan field. [9] These are presented in Table 1. The two water types differ significantly by their total salinity and the concentrations of the divalent ions. For a reference point, the composition of seawater is also included. This represents the ultimate endpoint for the compositions of water produced from water flooded wells.

End-member Typical occurrence		Na⁺ mg/L	K⁺ mg/L	Mg <sup>2+</sup> mg/L	Ca²+ mg/L	Sr <sup>2+</sup> mg/L	Ba²+ mg/L	Cl- mg/L	SO <sub>4</sub> ²- mg/L
Halfdan N	Mean	15931	154	210	891	91	12	27003	42
Halfdan S	Mean	26648	210	408	2611	328	1.0	47023	560
Seawater [12]	-	10780	400	1280	410	20	0.0	19350	2710

Table 1: Composition of water types identified at the Halfdan field and seawater. From [9].

### 2 Materials and methods

### **2.1** Samples and storage

61 samples from the Halfdan field in the Danish North Sea are included in the presented study. These have been collected from 23 different wells, distributed all across the field and were collected from June 2018 to March 2019. The sampling protocol is described in details in "Bergfors *et al.*, 2020". [11] In both papers, the samples are referred to as DNS (DHRTC New Samples). Importantly, all samples were collected at the test separators and none of the samples were treated after collection. In the work presented in this paper, the samples are divided into two groups: Samples from the northern part (N) and samples from the southern part (S) of the Halfdan field, respectively. This is illustrated in Figure 1. Samples from North cover 29 samples and from South 32 samples.



**Figure 1**: Map of the Halfdan field. From the Danish Energy Agency. [13] Information on scale observations and predictions has been added by the authors. The information is based on observations reported by the field operator (observations) combined with results presented by Bergfors *et al.* [11] 4

All samples were analyzed the first time within one week of arrival to the DHRTC laboratory (approximately three weeks after sampling). Following the transportation, the samples were stored in blue cap bottles, in a dark refrigerator at 5°C. A year after the initial analysis, the samples were re-analyzed following the exact same analytical protocol as the first analysis. All steps including sample preparation were repeated.

In the presented work, parity plots are used to compare the experimental results. In the parity plot, the one-to-one correlation is shown with dashed line and the  $\pm 25\%$  deviations from the one-to-one correlation with a full line. In the comparison and discussion, only points within the  $\pm 25\%$  deviation are included.

### **2.2** Sample preparation and analysis

The pH of all samples was measured immediately after arrival to the laboratory using a simple pH strip.

Prior to the analysis, the samples were filtered using a  $0.2 \,\mu$ m nylon filter to remove potential particles and diluted. Two analytical techniques were used: For the ICP-OES analysis, the samples were diluted 70-fold using 2% HNO<sub>3</sub> and for the IC analysis, the samples were diluted 100-fold using Milli-Q water.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) is used for the analysis of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup>. The instrument is an iCAP<sup>TM</sup> 7200 from Thermo Fischer Scientific. It has an Echelle optical design and a Charge Injection Device (CID) solid-state detector. The latter is kept cold by thermoelectric cooling with a ThermoFlex<sup>TM</sup> 900 recirculating chiller from Thermo Fischer Scientific. The ICP-OES is equipped with a concentric nebulizer and a cyclonic spray chamber. It is provided with pure Ar(g) (N6.0) for both purging and the plasma. An ASX-560 autosampler from Teledyne CETAC Technologies is used for sample uptake.

Ion Chromatography (IC) is used for the analysis of Cl<sup>-</sup> and SO<sub>4</sub><sup>2</sup>, as only cations can be analysed using ICP-OES. The instrument is a Dionex IonPac<sup>TM</sup> AS22, RFIC<sup>TM</sup>, with a 4 x 250 mm column. It has an IonPac<sup>TM</sup> CG16-4m, RFIC<sup>TM</sup>, 4 x 50 mm guard column. The eluent contains 4.5 mM sodium carbonate and 1.5 mM sodium bicarbonate and is prepared from Dionex<sup>TM</sup> AS22 Eluent concentrate.

Further details on the experimental workflow are provided in "Bergfors et al., 2020". [11]

### **3** Results and discussion

### 3.1 Compositional changes

Looking at the physical samples, no changes are observed; no *visible* precipitation, nor gas formation (for example  $H_2S$ ) is observed. However, this does not necessarily mean nothing has happened. The smell of  $H_2S$  (g) may be hidden behind the light smell from oil traces in the water; and precipitation can have occurred in amounts too small to be observed with the human eye. For all samples, the measured pH was in the range of 7-8 at the time of arrival to the laboratory. The slight alkaline pH suggests that the samples have already equilibrated with the atmosphere (CO<sub>2</sub> converting to HCO<sub>3</sub><sup>-</sup> in solution).

From the chemical analysis, we observe only minor changes in the composition of the samples. Figure 2 and 3 show the changes in the ionic concentrations from the analyses in 2018/2019 to 2020. Figure 2 presents the % change with the initial measurements (2018/2019) taken as the reference value. Figure 3 shows parity plots with the measured concentrations in 2018/2019 and 2020, respectively. The parity plot linear trendline equations and their regression coefficients are given in Table 2.

From Figure 2, it is found that most of the elements do not show one clear trend of either decrease or increase with time. The most consistent change is observed for Na<sup>+</sup>, which generally increases ( $\leq 10\%$  for the majority of the samples). Interestingly, SO<sub>4</sub><sup>2-</sup> shows a few extreme changes: 7 of the 61 samples (11%) show an increase in the SO<sub>4</sub><sup>2-</sup> concentration above 100%, which are explained by erroneous (too low) measurements in 2018/2019 (this is more clearly seen in the parity plot presented in Figure 3).

According to the trendline slopes, all ions except  $Sr^{2+}$  and  $SO_{4^{2-}}$ , are depleted within that one year between analyses. However, for Na<sup>+</sup>, Mg<sup>2+</sup> and Ba<sup>2+</sup>, the slopes are  $\geq 0.94$ , suggesting no significant change has occurred. Good agreement between the measured values and the reported water types given in Table 1 is observed. For K<sup>+</sup>, the slope is 0.81 and for Ca<sup>2+</sup> it is 0.66. These slopes are significant and suggest an actual change has occurred, however for K<sup>+</sup>, the measured concentrations plot in good agreement with both the reported water types observed at the Halfdan field. Generally, a decrease in concentration can be explained as precipitation. Both K<sup>+</sup> and Ca<sup>2+</sup> will most like precipitate as chloride salts. Plots of the change in concentrations of K<sup>+</sup> and/or Ca<sup>2+</sup> vs. the Cl<sup>-</sup> concentration change do not show a correlation between the decreases in the difference ions. Instead, we argue the decrease in Ca<sup>2+</sup> is caused by precipitation of CaCO<sub>3</sub>, due to the equilibration with the relative larger concentration of  $CO_2(g)$  available in the ambient atmosphere as compared to a reservoir environment. Also, the measured Ca<sup>2+</sup> concentrations agree only with water type Halfdan North. Water type Halfdan South shows significantly higher Ca<sup>2+</sup> levels than those observed, suggesting a loss of Ca<sup>2+</sup> prior to the analysis.

All the measured Cl<sup>-</sup> concentrations plot very closely, suggesting no regular changes. Furthermore, the Cl<sup>-</sup> concentrations are in agreement with water type Halfdan North, which again suggest that the Cl<sup>-</sup> concentrations are stable over time.



Figure 2: Change in sample composition [DHRTC New Samples (DNS) and Operator New Samples (ONS)] after one year of being stored. 7

The trend for  $SO_{4^{2-}}$  reported in Table 2 only includes 50% of the measurements. This trend suggests no changes in the  $SO_4^{2-}$  concentrations (slope of trendline = 1.022). The excluded points mainly plot at low 2018/2019 concentrations. The concentrations determined in 2020 corresponds better with the expected values; as water flooding is employed at the Halfdan field and the samples are recent, SO42concentrations close to the level found in seawater ( $\approx 2700 \text{ mg/L}$ ) is expected. In Part 1, several of the  $SO_4^{2-}$  concentrations were found to be lower than the reported data for nearly identical samples. Thus, we suggest that the excluded points represent erroneous measurements in 2018/2019. Despite strictly following the experimental protocols, we expect outliers resulting from ion loss due to eg. precipitation and/or a combination of deviations in the sample handling. An increase in ionic concentrations can only happen through evaporation. However, upon water evaporation, the increase in the ionic concentration would be observed across all ions. No signs of evaporation in a scale that could lead to significant changes in the ionic concentrations were observed. Additionally, all points included in the trend agree well with the reported water types identified at the Halfdan field.

Ion	Linear trendline	Regression coefficient	Number of points	Absolut average
	a x + b	R <sup>2</sup>	excluded from the	deviation
			trend	(trend/all points)
Na+	0.9618 x + 1276.5	0.816	2 (3%)	7%/8%
K <sup>+</sup>	0.8101 x + 29.271	0.8087	10 (17%)	12%/17%
Mg <sup>2+</sup>	0.9671 x + 7.4439	0.9585	9 (10%)	11%/18%
Ca <sup>2+</sup>	0.6648 x + 256.06	0.8861	12 (20%)	10%/15%
Sr <sup>2+</sup>	1.0532 x - 0.0629	0.8621	5 (8%)	9%/15%
Ba <sup>2+</sup>	0.9368 x + 0.0237	0.9832	9 (15%)	22%/61%
Cl-	No regular t	rend observed	-	18%
SO <sub>4</sub> <sup>2-</sup>	1.022 x <b>-</b> 16.111	0.9691	29 (48%)	8%/80%

**Table 2:** Effect of one year storage on ionic composition of produced water samples: Linear trendline equations and their regression coefficients for the parity plots shown in Figure 9. The value measured first (2018/2019) is taken as reference (x). The absolut average deviation (AAD) reported is determined based on the information provided in Figure 2. Left: AAD from points included in the trend, right: AAD from all measured points.



**Figure 3**: Parity plots illustrating the change in sample composition [DHRTC New Samples (DNS) and Operator New Samples (ONS)] after one year of being stored. The solid lines represents the ±25% deviation from a one-to-one correlation, which is marked by the dotted line. The compositions of the water types are given in Table 1.

### 3.2 Experimental precautions

To ensure an accurate determination of all ions, the following precautions have been taken (both in 2018/2019 and 2020; nothing is done differently): A stable signal in the IC detector has been ensured before the analysis has begun (only applicable for the IC analysis); a quality control is run for every ten samples; a new eluent (IC) and internal standard (ICP-OES) were prepared at the beginning of every analysis; and, the analyses have been done on several days, with new calibration standards prepared every day. No carry-over between analyses has been observed (checked by running blanks randomly distributed in the sequence). Furthermore, no changes have been done to the set-up (eg. change in column or configuration of the system) has been done between the 2018/2019 analyses and the 2020 analyses. Thus, all precautions have been taken and the reason for the erroneous points (those that are excluded from the trends) cannot be located. The observed variations could be a result of several events including subsampling and handling, variations in response factors and presence of salt crystals.

The authors are aware that the composition reported in this work does not sum up to a neutral solution. However, no correlation between points plotting off-trend and solutions with high charge imbalance is observed. This is illustrated in the Supplementary Material, Figure A.1. Additionally, no trend between the location/well of a sample and points plotting off-trend is observed.

### 3.3 Impact of findings

The time of storage is found to cause minor changes in the compositions of the samples. The concentrations of Na<sup>+</sup>, Mg<sup>2+</sup>, and Ba<sup>2+</sup> are found to decrease slightly ( $\leq 6\%$ ). While the changes in the concentrations of K<sup>+</sup> and Ca<sup>2+</sup> are significant (with 19% and 34%, respectively). The loss of Ca<sup>2+</sup> may be caused by formation of CaCO<sub>3</sub>. Thus, to limit the effect of time, it is suggested that it is prioritized the produced water samples are analyzed shortly after they have been collected. Sample bottles should be match the volume of the samples to limit the air volume in the bottle.

Furthermore, the samples should be stored cold ( $5^{\circ}$ C) if possible to slow the kinetic as much as possible (eg. precipitation). This way, the analyzed samples will be as representable as possible. Optimally, the samples are to be analyzed at the production site, which is difficult at offshore platforms.

The presented findings suggests that produced water samples maintain a lot of their value despite time passing by. This is very fortunate, as samples may be advantageous to analyze significantly later than sampled to gain further information.

The samples included in this study have not been preserved with acid at any time after sampling. Despite this, no change in the  $SO_4^{2-}$  is observed, suggesting that microbial activity do not affect the sample significantly. However, preservation may have other reasons than to limit microbial activity, thus may still be advantageous. If so, the preservation method must match *why* preservation is needed. Additionally, the preservation technique should be reported in details.

To take this study further, two approaches are suggested: 1) Filtrate the samples and analyze the filtride to investigate the impact of inorganic scale crystals and 2) digest the samples prior to analysis. Both approaches may help reveal the sink for  $K^+$  and  $Ca^{2+}$ .

### 4 Concluding remarks

Minor changes in the sample composition of 61 individual samples are observed as a consequence of long-time (one year) storage. The concentrations of Na<sup>+</sup>, Mg<sup>2+</sup> and Ba<sup>2+</sup> are found to decrease, but insignificantly ( $\leq 6\%$ ). K<sup>+</sup> and Ca<sup>2+</sup> are found to decrease more significantly; with 19% and 34%, respectively. The cause have not been identified and confirmed experimentally. The concentrations of SO<sub>4</sub><sup>2-</sup> and Sr<sup>2+</sup> are found to increase insignificantly ( $\leq 5\%$ ). Fortunately, the presented findings suggest that the samples maintain much of their information and, by this, may be valuable in case of need for later analysis. In conclusion, we have shown that the common notion that produced water sample compositions cannot be trusted for samples older than a month is incorrect, even when samples are not stored under special conditions.

### 5 Acknowledgements

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# Produced water from the North Sea – A case study and analytical guidelines Part 2: Impact of storage

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### Supplementary information
### 1. Charge balance



Figure A.1: Calculated charge balance from the measured ionic compositions.

## A.4 Experimental protocols

This is an experimental protocol describing, step-by-step, how sample preparation, solution preparation (calibration standards and quality controls), and the ICP-OES analysis of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Ba<sup>2+</sup> and Sr<sup>2+</sup> are carried out. The solution preparation and sample preparation cover both the ICP-OES of cations and IC analysis of Cl<sup>-</sup> and SO<sup>2-</sup><sub>4</sub>. Also, an overview of required ICP-OES maintenance is provided. I have made all the attached protocols. Annette E. Jensen tested the protocols and provided valuable feedback. A guide to the IC analyses is not included as these analyses follow the general guidelines provided in the DHRTC laboratory.

In the protocol describing the ICP-OES analysis, LabGuru is mentioned. LabGuru is an Electronic Laboratory Notebook, that was implemented in the laboratories at DHRTC in 2017. This is used to store all experimental data including daily notes.

2019

# Sample preparation: Analysis of produced water

STEP-BY-STEP GUIDE SOFIE NITSCHE GOTTFREDSEN Sample preparation sgott

#### First step: Filtration and 10-fold dilution

For all samples, this is the first thing that must be done.

Filtration:

- Attach a nylon 0.2 ym filter to a syringe
- Take up approximately 2 mL sample
- Detach the filter and syringe
- Press the sample into a small beaker (20 mL)

10-fold dilution:

- Name each tube according to the sample
- Take 1 mL sample and add to a test tube (10 mL)
- Add 9 mL MilliQ water
- Put a lid on the tube and mix it well (turn it upside-down 10 times)

Mark the samples with date and dilution factor.

#### IC analysis of SO42- and Cl-

A 100-fold dilution must be made from the 10-fold diluted, filtered sample:

- Name each tube according to the sample
- Take 0.05 mL 10-fold diluted sample and add to a test tube (5 mL)
- Add 4.95 mL MilliQ water
- Put a lid on the tube and press it down halfway
- Mix it well (turn it upside-down 10 times)
- Press the lid fully down

The total dilution factor is 1000 and the total volume is 5 mL.



January 2019

Sample preparation sgott

#### ICP-OES analysis of Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and K<sup>+</sup>

A 7-fold dilution must be made from the 10-fold diluted, filtered sample:

- Name each tube according to the sample
- Take 1 mL 10-fold diluted sample and add to a test tube (10 mL)
- Add 6 mL 2% HNO<sub>3</sub>
- Put a lid on the tube and mix it well (turn it upside-down 10 times)

The total dilution factor is 70 and the total volume is 7 mL.

#### ICP-OES analysis of Ba<sup>2+</sup> and Sr<sup>2+</sup>

A 7-fold dilution must be made from the 10-fold diluted, filtered sample:

- Name each tube according to the sample
- Take 1.5 mL 10-fold diluted sample and add to a test tube (10 mL)
- Add 9 mL 2% HNO<sub>3</sub>
- Put a lid on the tube and mix it well (turn it upside-down 10 times)

The total dilution factor is 70 and the total volume is 10.5 mL.





2019

# Solution preparation: IC and ICP-OES analysis

STEP-BY-STEP GUIDE SOFIE NITSCHE GOTTFREDSEN

#### **ICP-OES** analysis

#### Wash: 2% HNO<sub>3</sub>

We prepare 2 L, 2% HNO<sub>3</sub> from a purchased 70% HNO<sub>3</sub> solution. This is used to dilute the calibration standards and samples, and to wash the tubing.

The following must be done in a fume cupboard and gloves must be worn.

- Prepare a 2 L volumetric flask and a 100 mL glass beaker.
- Collect the 70% HNO<sub>3</sub> solution.
- Fill the volumetric flask with MilliQ water until it is 2/3 full.
- Pour approximately 60 mL 70% HNO<sub>3</sub> into the glass beaker.
- Transfer 52.7 mL 70% HNO<sub>3</sub> into the volumetric flask.
- Fill the volumetric flask with MilliQ water to the mark.
- Homogenize the solution: Turn it upside down ten times.
- Dispose the remaining 70% HNO<sub>3</sub> and wash the glass beaker with plenty of water.
- Leave the glass beaker for wash.
- Mark the flask with "The product is not labeled in accordance to regulation...", content with concentration and date.

#### Wash: 4% HNO<sub>3</sub>

We prepare 1 L, 4% HNO<sub>3</sub> from a purchased 70% HNO<sub>3</sub> solution. This is used to wash the tubing.

The following must be done in a fume cupboard and gloves must be worn.

- Prepare a 1 L volumetric flask and a 100 mL glass beaker.
- Collect the 70% HNO<sub>3</sub> solution.
- Fill the volumetric flask with MilliQ water until it is 2/3 full.
- Pour approximately 60 mL 70% HNO<sub>3</sub> into the glass beaker.
- Transfer 52.7 mL 70% HNO<sub>3</sub> into the volumetric flask.
- Fill the volumetric flask with MilliQ water to the mark.
- Homogenize the solution: Turn it upside down ten times.
- Dispose the remaining 70% HNO<sub>3</sub> and wash the glass beaker with plenty of water.
- Leave the glass beaker for wash.
- Mark the flask with "The product is not labeled in accordance to regulation...", content with concentration and date.

#### ICP-OES analysis of Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and K<sup>+</sup>

#### Internal standard: 50 ppm Y<sup>2+</sup>

We prepare 250 mL, 50 ppm  $Y^{2+}$  in 2% HNO<sub>3</sub> from a purchased 1 000 mg/L  $Y^{2+}$  solution.

- Prepare a 250 mL volumetric flask and a 250 mL blue cap bottle.
- Collect the 1 000 mg/L Y<sup>2+</sup> solution.
- Homogenize it: Turn it upside-down ten times.
- Transfer 12.5 mL concentrated Y<sup>2+</sup> solution into a 250 mL volumetric flask.
- Fill the volumetric flask with 2% HNO<sub>3</sub> to the mark.
- Homogenize the solution: Turn it upside down ten times.
- Transfer the solution into a blue cap bottle.
- Mark the bottle with "The product is not labeled in accordance to regulation...", content with concentration and date.

The internal standard must be prepared at least once a month.

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#### Calibration stock solution

The calibration standards are made from a homemade stock solution. The stock solution must be made at least once a month.

Make the stock solution – 250 mL

- Prepare a 250 mL volumetric flask and a 250 mL blue cap bottle.
  - Collect the needed elemental standards:
    - 10 000 mg/L Na⁺,
    - $\circ$  10 000 mg/L Mg<sup>2+</sup>,
    - o 10 000 mg/L Ca<sup>2+</sup>,
    - 0 10 000 mg/L K<sup>+</sup>,
    - o 2% HNO<sub>3</sub> (min. 250 mL).
- Homogenize the elemental standards: Turn them upside-down ten times.
- Add the appropriate volumes of the elemental standards to the volumetric flask:

250 mL stock	Final concentration, ppm	Volume, mL
Na <sup>+</sup>	3000	75
Ca <sup>2+</sup>	100	2.5
Mg <sup>2+</sup>	70	1.75
K⁺	10	0.25

- Fill the volumetric flask with 2% HNO<sub>3</sub> to the mark.
- Homogenize the solution: Turn it upside-down ten times.
- Transfer the solution to a 250 mL blue cap bottle.
- Mark the bottle with "The product is not labeled in accordance to regulation...", content with concentration and date.

The stock solution must be stored in the fridge at 5°C.

#### Calibration standards

The calibration standards are prepared from the stock solution.

- Prepare four 50 mL test tubes (see picture below).
- Name them eg. "C1", "C2"... and mark with date.
- Transfer the needed amount of stock solution into each test tube:

	C1	C2	C3	C4
Dilution factor	x50	x20	x10	x5
Na⁺, ppm	60	150	300	600
Mg <sup>2+</sup> , ppm	1.4	3.5	7	14
Ca <sup>2+</sup> , ppm	2	5	10	20
K⁺, ppm	0.2	0.5	1	2
Stock volume, mL	1	2.5	5	10
2% HNO <sub>3</sub> , mL	49	47.5	45	40

- Add the needed amount of 2% HNO<sub>3</sub> (see table above).
- Put a lid on the tubes and homogenize them: Turn them upside-down ten times.

The standards must be prepared at least once a week.



#### <u>QCs</u>

The QCs are prepared from the purchased MultiElement 3 standard solution.

- Prepare two 50 mL test tubes (see picture below).
- Name them eg. "QC1", "QC2" and mark with date.
- Transfer the needed amount of MultiElement 3 solution into each test tube:

	QC1	QC2
Dilution factor	x20	x100
MultiElement 3, mL	2.5	0.5
2% HNO₃, mL	47.5	49.5

- Add the needed amount of 2% HNO<sub>3</sub> (see table above).
- Put a lid on the tubes and homogenize them: Turn them upside-down ten times.

The QCs must be prepared at least once a week.



#### ICP-OES analysis of Ba<sup>2+</sup> and Sr<sup>2+</sup>

#### Internal standard: 10 ppm Sc<sup>2+</sup>

We prepare 250 mL, 10 ppm  $Sc^{2+}$  in 2% HNO<sub>3</sub> from a purchased 1 000 mg/L  $Sc^{2+}$  solution.

- Prepare a 250 mL volumetric flask and a 250 mL blue cap bottle.
- Collect the 1 000 mg/L Sc<sup>2+</sup> solution.
- Homogenize it: Turn it upside-down ten times.
- Transfer 2.5 mL concentrated Sc<sup>2+</sup> solution into a 250 mL volumetric flask.
- Fill the volumetric flask with 2% HNO<sub>3</sub> to the mark.
- Homogenize the solution: Turn it upside down ten times.
- Transfer the solution into a blue cap bottle.
- Mark the bottle with "The product is not labeled in accordance to regulation...", content with concentration and date.

The internal standard must be prepared at least once a month.

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#### Calibration stock solution

The calibration standards are made from a homemade stock solution. The stock solution must be made at least once a month.

Make the stock solution – 250 mL

- Prepare two 100 mL volumetric flasks, a 250 mL volumetric flask and a 250 mL blue cap bottle.
  - Collect the needed elemental standards:
    - o 10 000 mg/L Na⁺,
    - o 10 000 mg/L Ba<sup>2+</sup>,
    - o 10 000 mg/L Sr<sup>2+</sup>,
    - o 2 % HNO<sub>3</sub> (min. 250 mL).
- Homogenize the elemental standards: Turn them upside-down ten times.
- Start by doing a 10-fold dilution of the Ba<sup>2+</sup> and Sr<sup>2+</sup> single element solutions. These are to be used for the stock solution. Do them separately in each their 100 mL volumetric flask:
  - Mark the flasks with "The product is not labeled in accordance to regulation...", content with concentration (1 000 ppm) and date.
  - $\circ~$  Add 10 mL of the elemental standard and fill the volumetric flask to the mark with 2% HNO\_3.
  - Homogenize the solutions: Turn them upside-down ten times.
- Add the appropriate volumes of the elemental standards to the volumetric flask:

250 mL stock	Final concentration, ppm	Volume, mL
Na⁺, 10 000 ppm	9000	225
Sr <sup>2+</sup> , 1 000 ppm	50	12.5
Ba <sup>2+</sup> , 1 000 pm	0.5	0.125

- Fill the volumetric flask with 2% HNO<sub>3</sub> to the mark.
- Homogenize the solution: Turn it upside-down ten times.
- Transfer the solution to a 250 mL blue cap bottle.
- Mark the bottle with "The product is not labeled in accordance to regulation...", content with concentration and date.

The stock solution must be stored in the fridge.

#### Calibration standards

The calibration standards are prepared from the stock solution.

- Prepare four 50 mL test tubes (see picture below).
- Name them eg. "C1", "C2"... and mark with date.
- Transfer the needed amount of stock solution into each test tube:

	C1	C2	C3	C4
Dilution factor	x100	x50	X20	X10
Na⁺, ppm	90	180	450	900
Sr <sup>2+</sup> , ppm	0.5	1	2.5	5
Ba <sup>2+</sup> , ppm	0.005	0.01	0.025	0.05
Stock volume, mL	0.5	1	2.5	5
2% HNO3, mL	49.5	49	47.5	45

- Add the needed amount of 2% HNO<sub>3</sub> (see table above).
- Put a lid on the tubes and homogenize them: Turn them upside-down ten times.

The standards must be prepared at least once a week.



#### <u>QCs</u>

We use the purchased MultiElement standard as QC.

This does not need any preparing and is transferred directly into a 50 mL tube:

- Prepare one 50 mL test tubes (see picture below).
- Name the tube eg. "MultiElement" and mark with date.
- Homogenize the MultiElement standard: Turn it upside-down ten times.
- Transfer approximately 50 mL into the test tube.

The QC must be changed at least once a week.



Solution preparation sgott

### IC analysis of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>

#### <u>Eluent</u>

Follow the instructions on the eluent concentrate bottle.

#### Calibration standards

The calibration standards are made from two purchased standards containing 1 000 mg/L Cl<sup>-</sup> and 1 000 mg/L SO<sub>4</sub><sup>2-</sup>, respectively. We start by doing a 10-fold dilution of the SO<sub>4</sub><sup>2-</sup> standard.

Make the 10-fold diluted single-elemental SO<sub>4</sub><sup>2-</sup> standard - 100 mL

- Prepare two 100 mL volumetric flasks and two 20 mL glass beakers.
- Collect the needed elemental standards:
  - o 1 000 mg/L SO4<sup>2-</sup>,
- Homogenize the elemental standard: Turn it upside-down ten times.
- Mark the volumetric flasks with "The product is not labeled in accordance to regulation...", content with concentration (100 mg/L) and date.
- Add 10 mL of one elemental standard to the volumetric flask.
- Fill the volumetric flask with MilliQ water to the mark.
- Homogenize the solution: Turn it upside-down ten times.

This 100 mg/L solution must be stored in the fridge and properly sealed. It must be prepared once a month.

You now have two options:

- Several analyses are to be run within the following week: Prepare a bulk of the calibration standards.
- One analysis is to be run within the following week: Prepare only one set of calibration standards.

Bulk - 50 mL of each standard

- Prepare four 50 mL volumetric flasks.
- Name them eg. "C1", "C2"... and mark with date.
- Transfer the needed amount of the 10-fold diluted single-elemental standard into each volumetric flask:

50 mL	Final concent	ration, mg/L	Volume,	, mL
	Cl-	SO4 <sup>2-</sup>	Cl <sup>-</sup> (1000 mg/L)	SO4 <sup>2-</sup> (100 mg/L)
C1	40	1	2.0	0.5
C2	60	2	3.0	1.0
C3	80	5	4.0	2.5
C4	100	10	5.0	5.0

- Fill the flasks with MilliQ water to the mark.
- Put a lid on the volumetric flasks and homogenize them: Turn them upside-down ten times.

These standards must be stored in the fridge and properly sealed. They must be prepared once a week.

Single standard – 5 mL in test tube

- Prepare four 5 mL test tubes (see picture below).
- Name them eg. "C1", "C2"...
- Transfer the needed amount of the 10-fold diluted single-elemental standard into each test tube:

5 mL	Final concent	ration, mg/L	Volu	me, μL	
	Cl⁻	SO4 <sup>2-</sup>	Cl <sup>-</sup> (1000 mg/L)	SO4 <sup>2-</sup> (100 mg/L)	MilliQ water
C1	40	1	200	50	4 750
C2	60	2	300	100	4 600
C3	80	5	400	250	4 350
C4	100	10	500	500	4 000

- Add the need amount of MilliQ water to each of the test tubes (see table above).
- Put the lids halfway on and homogenize the standards: Turn them upsidedown ten times.
- Press the lids fully on.



Page **11** of **14** 

#### QC solutions

The QC solutions are prepared from the purchased Dionex<sup>™</sup> Combined Five Anion Standard.

You now have two options:

- Several analyses are to be run within the following week: Prepare a bulk of the QC solutions.
- One analysis is to be run within the following week: Prepare only one set of QC solutions.

Bulk – 50 mL of each QC solution

- Prepare two 50 mL volumetric flasks.
- Name them eg. "QC1" and "QC2" and mark with date.
- Transfer the needed amount of the Five Anion Standard (5+ std) into each volumetric flask:

50 mL	Final concentrat	Final concentration, mg/L	
	Cl	SO4 <sup>2-</sup>	5+ std
QC1	0.03	0.15	50
QC2	0.3	1.5	500

- Fill the flasks with MilliQ water to the mark.
- Put a lid on the volumetric flasks and homogenize them: Turn them upside-down ten times.

These standards must be stored in the fridge and properly sealed. They must be prepared once a week.

#### Single set of QC solutions – 5 mL in test tube

- Prepare the needed amount of test tubes (see picture below):
  - For every ten samples, one set is prepared plus one to start with.
  - Eg: 30 samples -> 3 + 1 = 4 sets.
- Name them eg. "QC1a", "QC2a", "QC1b", "QC2b"...
- Transfer the needed amount of the Five Anion Standard (5+ std) into each test tube:

5 mL	Final concentr	ation, mg/L	Volume, μL	
	Cl	SO4 <sup>2-</sup>	5+ std	MilliQ water
QC1	0.03	0.15	5	4 995
QC2	0.3	1.5	50	4 950

- Add the need amount of MilliQ water to each of the test tubes (see table above).
- Put the lids halfway on and homogenize the standards: Turn them upside-down ten times.
- Press the lids fully on.



Content	Concentration	Amount	Supplier	Product no.
Dionex™ AS22 Eluent		250 mL	Thermo	063965
Concentrate			Scientific	
Cl in water	1 000 mg/L	100 mL	Sigma Aldrich	39883-100ML
SO4 in water	1 000 mg/L	100 mL	Sigma Aldrich	90071-100ML
Dionex <sup>™</sup> Combined Five		100 mL	ThermoFischer	037157
Anion Standard			Scientific	
iCAP 6000 Set Up	2 ppm Zn	500 mL	ThermoFischer	430122821411
Solution (loaded blank)			Scientific	
MultiElement standard		100 mL	Sigma Aldrich	49596-100ML
solution 3 for ICP in 5%				
HNO₃				
iCAP 6000 Multi-Element		500 mL	ThermoFischer	430122821401
Test Solution			Scientific	
Na std, in 5% HNO₃	10 000 mg/L	500 mL	VWR	ACSDC135.2NP.L5
Mg std, in 5% HNO₃	10 000 mg/L	100 mL	VWR	455634F
Ca std, in 2-5% HNO₃	10 000 mg/L	100 mL	VWR	455174V
K std, in 2-3% HNO₃	10 000 mg/L	100 mL	VWR	455832J
Ba std, in 2-5% HNO₃	10 000 mg/L	100 mL	VWR	455072Q
Sr std, in 2-5% HNO₃	10 000 mg/L	100 mL	VWR	456072U
Sc std in 2-5% HNO <sub>3</sub>	1 000 mg/L	100 mL	VWR	456872V
Y std in 2-5% HNO <sub>3</sub>	1 000 mg/L	100 mL	VWR	456982D
70 % HNO <sub>3</sub>	70 %	500 mL	Sigma Aldrich	438073-500ML

2019

# **ICP-OES** analysis

STEP-BY-STEP GUIDE SOFIE NITSCHE GOTTFREDSEN

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#### Preparing the instrument

Turn on the argon (if not already) and ensure that the pressure is 5.5 bar. Adjust if not.





OBS: The argon must be turned on <u>two hours</u> before the instrument. Preferably, it is turned on the day before the analysis. (It can be left on overnight, just ensure there is a minimum of one full flask available.)

If this time is not available – engineer purge must be on for 30 min.



Turn on the cooler:

OBS: The cooler must have had a stable temperature (18°C) for 15 min. before the ICP-OES instrument is turned on. From turning on the cooler to the instrument is ready for use, it takes approximately <u>30 min</u>.

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Turn on the suction (punktsug 2) for the autosampler (it is behind the autosampler cover):





Turn on the suction (punktsug 3) for the instrument (it is on the opposite side of the desk):

#### Turn on the autosampler:



Check that the tubes are uniform and has no deposits inside (particularly the parts of the tubes that are attached to the pump wheel).

If the tubes are not approved, they must be changed.

Attach the tubes to the pump wheel: Make sure they are placed correctly (colors from inside and out):

- 1: Sample introduction (orange-white) [running in]
- 2: Internal standard introduction (orange-blue) [running in]
- 3: Waste outlet (white-white) [running out]





January 2019



Make sure the tubing is shaped in a double loop after the Y-joining piece.

The design of the autosampler:



Rack: 1 Rack: 2 Rack: 3 Rack: 4

<u>Warm up</u>

In the standard rack, place the following:

Vial 1: MilliQ water. Vial 2: 2% HNO<sub>3</sub>.

Take the lids off.

Check that there are no droplets inside the spray chamber. If there is, clean it (see document on maintenance).



Click on the "Get started" icon.

When it is - press "OK".



Page **5** of **19** 

Check that the flow is smooth – if not, adjust.

Check that the spray from the nebulizer is uniform and creates a uniform mist inside the spray chamber.



Allow the warm up to finish.

ard	Dashbasa tak
ks	Dashboard - iCap7000 ASX 560
les	Clear Spectrometer Optimization 0% complete: 00:00 Stiticroses
ment	CARGON
(Query	Rame Rack 1 21-Vale (2/3)

#### Daily Zn control

In the standard row of the autosampler, place the following:

Vial 10: 2 ppm Zn.

Take the lid off.

Note the volume of Zn in LabGuru for later use.



Adjust the information:

Name = date, what is on the internal standard line. Position: Rack = Standard, Vial = 10.

Press "run" 🜔 and click "OK".

Wait until the run has completed.

Note the final Zn consumption in "2019\_Zn-volume". (<u>https://my.labguru.com/knowledge/experiments/914</u>) Note for one run only – if you do several runs, note the Zn consumption for each of the runs.

January 2019

Check the intensities: —

Proceed only if the radial intensity is 1 800 cps or higher and the axial intensity is 20 000 cps or higher.

If these criteria are not met, the glassware must be cleaned (see separate document on maintenance).



sgott Set up LabBook Choose "LabBooks" 20 LabBooks Dashboard Name the new LabBook: Create LabBook "yyyy-mm-dd\_sample-type\_analytes\_initials". LabBooks Create a new La Eg: 2019-01-01\_PW\_Ba-Sr\_sgott Templates 2019-01-23\_PW\_Na-Mg-Ca-K Method LabBooks\2019\Na-Mg-Ca-K (PW = Produced water) ment Create a new LabBook from an existing Te LabBook Query 2017-08-30\_FW-23 Import from CSV File Manager System Log Choose "Create a new LabBook from an existing LabBook". 2019-01-18\_PW\_Na-Mg-Ca-K te a new LabBook from a blank Tem Use Method De For Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, K<sup>+</sup> analysis, choose "2019\_Na-Mg-Ca-K". Open LabBook For Ba<sup>2+</sup> and Sr<sup>2+</sup> analysis, choose "2019\_Ba-Sr". Browse using the "..." bottom. 0017 1 Press "Create LabBook".

Click on "Sample list"

**ICP-OES** analysis

Adjust the information to fit the samples.

Follow the template sequence: 9 x sample, 1 x QC (change between QC1 and QC2), 1 x 2% HNO<sub>3</sub> wash, and repeat until finish.

End the sequence with one Wash 4% HNO<sub>3</sub> followed by a Wash 2% HNO<sub>3</sub>.

January 2019

#### Create the experiment in LabGuru

Open "2019\_ICP-analysis" (https://my.labguru.com/knowledge/protocols/99)

Press " Start experiment".

Choose the right path for the file: Eg. sgott\_ProducedWater/2019.

Name the file as the Qtegra file.

Press "Add experiment".

Follow the instructions in the template.

Remember to link to the relevant experiments and samples.

ICP-OES analysis sgott

#### Start the analysis

Transfer the internal standard (IS) introduction tube from the 2% HNO<sub>3</sub> wash to the internal standard.



Allow it to run for a few minutes.

Check there is enough washing liquid (2/3 is enough for a full day) – if not, fill it up (2% HNO<sub>3</sub>).

Note the temperature in LabGuru. (in/out)



Press "run" 🜔 and click "OK"

OBS: Follow the experiment continuously.

Note the temperature in LabGuru at the end of the experiment.

ICP-OES analysis sgott

#### Check the results

At the end of an analysis, the results are quality checked.

Click on "Intensities".

Do the intensities of the samples lie in the range of the intensities of the calibration standards?

If yes – the analysis is successfully done.

If no – one of two options must be applied:

Add another calibration standard to expand the covered range. Dilute the sample(s) differently to fit the covered range.

ICP-OES analysis sgott

#### Instrument shut-down

Transfer the IS-introduction tube from the internal standard to the 2% HNO<sub>3</sub> wash.

Allow it to run for a few minutes.



Press "Get started" and "Shut Down".

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ratal_Ze 2019-01-23_PV(_tast	MyCex
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112.03	
liane	Protest
	1 Part Participant

Allow the instrument to stop.

### Turn off the cooler:





Detach the tubes from the pump wheel.

It is a good idea to place the buckle in the way of the covers to ensure they do not fall down.





January 2019

#### Turn off the autosampler:





Turn off the suction (punktsug 3) for the instrument (press top of botton) (it is on the opposite side of the desk):



Turn off the suction (punktsug 2) for the autosampler:


ICP-OES analysis sgott

Turn off the computer screen. Lock the computer ("Windows" + L). Every Friday, the computer is turned off.

Turn off the argon if analyses are not to be run the following day.





Empty the water container.



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#### Export data/results

The data must be exported from the laboratory computer to the O-drive when the analysis is successfully finalized. The O-drive cannot to accessed directly on the laboratory computer, hence, a USB-stick must be used to transfer the data from the laboratory computer to any other computer with full internet access.

Plug in the USB-stick to the laboratory computer. We use encrypted USB-sticks.

Type in your password for the stick.

In Qtegra, open the experiment from which the data is to be exported.

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Two datasets are exported: One containing the results and one containing the calibration data.

Click on "Export ...'

January 2019

ICP-OES analysis sgott

Tick the boxes "Intensities" and "Concentrations". Check that the Export Path is correct – adjust if not. Name the file "*name-of-Qtegra-file\_*int-conc". Click "Export".



This picture will show – that is okay. You did it correctly. Just close the browser window.

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Tick the box "Calibration Information", all calibration data boxes will then be automatically ticked.

ICP-OES analysis sgott

Check that the Export Path is correct – adjust if not.

Name the file "name-of-Qtegra-file\_cali".

#### Click "Export".



This picture will show – that is okay. You did it correctly. Just close the browser window.

Mary Pare March 241, Correct 24	E 2019-01-27 Phy harke-Cark	2019_Ne-Mp-Ce-K	2019_B+-Sr	zonsosof_Neteriz	2019-02-01_PM
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Close down the USB-stick and unplug it.

Transfer the data using another computer to: O:\CONFIDENTIAL\WaterData\Analysis



# **ICP-OES** maintenance

GUIDE SOFIE NITSCHE GOTTFREDSEN ICP-OES analysis sgott

What	How often	How
Check tubing	Daily	
Torch alignment	Daily	Click box on when warming up
		the instrument
Spectrometer optimization	Once a month	Click box on when warming up
		the instrument
Change tubing	When needed	
Change chiller liquid	Every 3-6 months	Manual p. 51 (add ca. 1 dl
		corrosion inhibitor)
Change chiller filter	Every 3-6 months	Remove old and place new
		(with black tuber ring).
Clean glassware: Torch,	When needed or min. every 6	Manual p. 49-50
nebulizer, spray chamber	months	
Clean POP-window	When needed or min. every 2	Manual p. 50
	months	
Full maintenance by	Yearly (November/December)	
ThermoFischer		
Change all tubing	At ThermoFischer maintenance	

Manual:



## **B** Appendix

## **B.1 Reagents**

Content	Concentration	Amount	Supplier	Product no.
Dionex <sup>TM</sup> AS22 Eluent		250 mL	Thermo Scientific	063965
Concentrate				
Cl in water	1 000 mg/L	100 mL	Sigma Aldrich	39883-100ML
SO4 in water	1 000 mg/L	100 mL	Sigma Aldrich	90071-100ML
Dionex <sup>TM</sup> Combined Five		100 mL	ThermoFischer Scientific	037157
Anion Standard				
iCAP 6000 Set Up Solution	2 ppm Zn	500 mL	ThermoFischer Scientific	430122821411
(loaded blank)				
MultiElement standard		100 mL	Sigma Aldrich	49596-100ML
solution 3 for ICP in 5% $HNO_3$				
iCAP 6000 Multi-Element		500 mL	ThermoFischer Scientific	430122821401
Test Solution				
Na std, in 5% HNO <sub>3</sub>	10 000 mg/L	500 mL	VWR	ACSDC135.2NP.L5
Mg std, in 5% HNO $_3$	10 000 mg/L	100 mL	VWR	455634F
Ca std, in 2-5% $HNO_3$	10 000 mg/L	100 mL	VWR	455174V
K std, in 2-3% $HNO_3$	10 000 mg/L	100 mL	VWR	455832J
Ba std, in 2-5% $HNO_3$	10 000 mg/L	100 mL	VWR	455072Q
Sr std, in 2-5% $HNO_3$	10 000 mg/L	100 mL	VWR	456072U
Sc std in 2-5% $HNO_3$	1 000 mg/L	100 mL	VWR	456872V
Y std in 2-5% $HNO_3$	1 000 mg/L	100 mL	VWR	456982D
70 % HNO <sub>3</sub>	20 %	500 mL	Sigma Aldrich	438073-500ML

 Table B.1: List of specifications of chemicals used in the experimental work.

### B.2 Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES)

#### B.2.1 Hardware

Disposable, graduated conical CID solid state detector Recirculating Note Catalog number 62.548.004 Thermo Fischer Scientific SARSTEDT AG & Co Teledyne CETAC Thermo Fischer Thermo Fischer Supplier Phthalate-free PVC tubes 50 mL tube ThermoFlex 900 SID  $CAP^{TM}$  7200 ASX-560 Name Autosampler Hardware 2 CP-OES Tubing Vial no. Chiller

Table B.2: List of specifications of the hardware used for ICP-OES analysis.

#### **B.2.2 Calibration curves**



**Figure B.1:** Calibration curves for  $Na^+$  and  $K^+$  with the ICP-OES. The different curves represent calibration curves used at different days.



**Figure B.2:** Calibration curves for  $Ca^{2+}$  and  $Mg^{2+}$  with the ICP-OES. The different curves represent calibration curves used at different days.



**Figure B.3:** Calibration curves for  $Sr^{2+}$  and  $Ba^{2+}$  with the ICP-OES. The different curves represent calibration curves used at different days.

#### B.2.3 Method development and testing

## Spectral interference testing: Wavelength and test sample compositions $\ensuremath{\text{Na}^+\text{-Mg}^{2+}}$

Elemental ion	Mode		Tested wa	velengths					
		nm							
Na <sup>+</sup>	Radial	303.237	589.592	818.326	-				
$Mg^{2+}$	Radial	202.582	279.553	280.270	285.213				

Table B.3: The mode and analytical wavelengths selected for a spectral interference test of Na<sup>+</sup> and  $Mg^{2+}$ .

		(	Con	cen	trati	on,	ppm	۱	
Na <sup>+</sup>	5	7	3	3	5	7	0	0	0
$Mg^{2+}$	5	3	7	0	0	0	3	5	7

 Table B.4: The concentrations of Na<sup>+</sup> and Mg<sup>2+</sup> in the prepared test solutions.

Na<sup>+</sup>-Ca<sup>2+</sup>

Elemental ion	Mode	Test	ed waveler	ngths			
		nm					
Na <sup>+</sup>	Radial	303.237	818.326	-			
$Ca^{2+}$	Radial	184.006	315.887	373.690			

Table B.5: The mode and analytical wavelengths selected for a spectral interference test of  $Na^+$  and  $Ca^{2+}$ .

						Con	cent	ratio	n,pp	m					
Na <sup>+</sup>	5	11	17	5	11	17	5	11	17	5	11	17	0	0	0
$Ca^{2+}$	0	0	0	3	3	3	5	5	5	7	7	7	3	5	7

**Table B.6:** The concentrations of  $Na^+$  and  $Ca^{2+}$  in the prepared test solutions.

#### $Ca^{2+}-Mg^{2+}$

Elemental ion	Mode	Teste	ed waveler	ngths				
		nm						
$Ca^{2+}$	Radial	315.887	373.690	-				
$Mg^{2+}$	Radial	202.582	279.553	280.270				

Table B.7: The mode and analytical wavelengths selected for a spectral interference test of  $Ca^{2+}$  and  $Mg^{2+}$ .

								(	Con	centr	ation	, ppr	n					
Ca <sup>2+</sup>	5	3	7	0	0	0	3	5	7	55	73	89	65	73	89	65	73	89
$Mg^{2+}$	5	7	3	3	5	7	0	0	0	5	5	5	20	20	20	40	40	40

**Table B.8:** The concentrations of  $Ca^{2+}$  and  $Mg^{2+}$  in the prepared test solutions.

#### $Na^+$ - $K^+$ - $Ca^{2+}$ - $Mg^{2+}$

Elemental ion	Mode		Tested wa	velengths	
			n	m	
Na <sup>+</sup>	Radial	330.237	589.592	818.326	-
K+	Radial	404.414	766.490	769.896	-
Ca <sup>2+</sup>	Radial	315.887	393.366	422.673	-
$Mg^{2+}$	Radial	202.582	279.553	280.270	285.213
Y+	Radial		371	.030	

**Table B.9:** The mode and analytical wavelengths included in the spectral interference tests of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>and Mg<sup>2+</sup>. Y<sup>+</sup> is used as internal standard.

Na <sup>+</sup> , ppm	K <sup>+</sup> , ppm	Ca <sup>2+</sup> , ppm	$Mg^{2+}$ , ppm
1	0.1	0.1	0.1
5	0.5	0.5	0.5
10	1.0	1.0	1.0
25	5.0	5.0	5.0
50	10	10	10
75	15	15	15
100	20	20	20

Table B.10: The concentrations of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> in the prepared test solutions.



#### B.2.4 Recorded emission spectre

**Figure B.4:** Recorded emissions spectre of the elements included in the ICP-OES analysis. The green ares is the integrated area, which the software uses to determine the intensity. The concentration is determined from the intensity.

#### B.2.5 Internal standard

Elemental ion		Conce	entration	in ppm	Ì
	T1	T2	Т3	T4	T5
Na <sup>+</sup>	8000	800	400	160	80
${ m Sr}^{2+}$	50	5.0	2.5	1.0	0.5
$Ba^{2+}$	0.5	0.05	0.025	0.01	0.005

Table B.11: The composition of the test solutions used for a test to find the best concentration of  $Sc^{2+}$  as internal standard.

Reference number	Supplier	Product name	Volume	Product number	Note
Vial no. 1	WR	Centrifugal tubes	50 mL	21008-240	Disposable,
Vial no. 2	SARSTEDT AG & Co	Tube	50 mL	62.548.004	graduated conical Disposable,
Vial no. 3	FALCON	Conical Tube	15 mL	352196	graduated conical High-clarity polypropylene,
Vial no. 4	Frisenette	Sample tube	15 mL	305002	disposable, conical Disposable,
					round bottom

#### B.2.6 Vials and tubes

Table B.12: List of the vials tested. Vial no. 2 was used in the sample analysis.

### B.3 Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)

#### B.3.1 Samples

Sample number	Location of sample	Sample number	Location of sample
Run 01		Run 02	
1	Dan	35	Dan
2	Dan	36	Dan
3	Dan	37	Dan
4	Dan	38	Kraka
5	Dan	39	Kraka
6	Dan	40	Kraka
7	Halfdan NE	41	Kraka
8	Halfdan NE	42	Kraka
9	Halfdan NE	43	Kraka
10	Halfdan NE	44	Kraka
11	Halfdan NE	45	Halfdan NE
12	Halfdan NE	46	Halfdan NE
13	Halfdan NW	47	Halfdan NW
14	Halfdan NW	48	Halfdan NW
15	Halfdan NW	49	Halfdan SE
16	Halfdan NW	50	Halfdan SE
17	Halfdan SE	51	Valdemar
18	Halfdan SE	52	Valdemar
19	Halfdan SE	53	Valdemar
20	Halfdan SE	54	Valdemar
21	Halfdan SE	55	Valdemar
22	Halfdan SE		
23	Halfdan SE		
24	Halfdan SE		
25	Halfdan SE		
26	Halfdan SE		
27	Halfdan SE		
28	Halfdan SW		
29	Halfdan SW		
30	Halfdan SW		
31	Halfdan SW		
32	Valdemar		
33	Valdemar		
34	Valdemar		

 Table B.13: List of samples included in the analysis of heavy metal using ICP-MS.

## B.4 Ion Chromatography (IC)

#### B.4.1 Hardware

Hardware	Name	Supplier	Catalog number	Note
Ion chromatograph	Dionex Integrion HPIC	Thermo Scientific		
Guard column	IonPac $^{TM}$ CG16-4m, RFIC $^{TM}$	Thermo Scientific		4 x 50 mm
Analytical column	Dionex <sup>TM</sup> IonPac <sup>TM</sup> AS22, RFIC <sup>TM</sup>	Thermo Scientific	064139	Anion analysis, 4 x 250 mm
Analytical column	Dionex $^{TM}$ lonPac $^{TM}$ CS16-4m	Thermo Scientific	088584	Cation analysis, 4 x 250 mm
Suppressor	Dionex $^{TM}$ AERS $^{TM}$ 500 Carbonate	Thermo Scientific	085029	Anion analysis, 4 mm
Suppressor	Eletrolytically Regenerated Suppressor Dionex <sup>TM</sup> ERS <sup>TM</sup> 500e Cation	Thermo Scientific	302663	Cation analvsis. 4 mm
:	Electrolytically Regenerated Suppressor			
Gradient mixer	Dionex $^{TM}$ GM-4	Thermo Scientific	049136	2 mm

 Table B.14: List of specifications of the hardware used for IC analysis.

#### B.4.2 Calibration curves



**Figure B.5:** Calibration curves for  $CI^-$  and  $SO_4^{2-}$  with the IC. The different curves represent calibration curves used at different days.



**Figure B.6:** Calibration curves for Na<sup>+</sup> and K<sup>+</sup> with the IC. The different curves represent calibration curves used at different days.



**Figure B.7:** Calibration curves for  $Ca^{2+}$  and  $Mg^{2+}$  with the IC. The different curves represent calibration curves used at different days.

#### B.4.3 Chromatograms



Figure B.8: Chromatograms of  $CI^-$  and  $SO_4^{2-}$  in a set of calibration standards.



Figure B.9: Chromatograms of  $CI^-$  and  $SO_4^{2-}$  in three different samples.



Figure B.10: Chromatograms of  $CI^-$  and  $SO_4^{2-}$  in three different samples.



Figure B.11: Chromatograms of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> in a set of calibration standards.



Figure B.12: Chromatograms of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> in three different samples.



Figure B.13: Chromatograms of Na<sup>+</sup>,  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  in three different samples.

#### **B.4.4 Sample preparation**

Hardware	Name	Supplier	Catalog number	Note
Water purification system	Milli-Q <sup>®</sup> Advantage A10	Merck Millipore		
Syringe	10 mL luer-lock	CHIRANA T. Injecta	CH03010LL	
Needle		Sterican, B. BRAUN		Polypropylene needle hub
Filter	25 mm syringe filter	fisher brand	15121499	Nylon filter

 Table B.15: List of specifications of the hardware used for the sample preparation.

## **B.5** Gas Chromatography x Gas Chromatography (GCxGC)

#### **B.5.1** Chemicals and reagents

Content	Name	Supplier
Benzoic acid		
N,O-bis(trimethylsilyl)trifluoroacetamide	Supelco	
containing 1% of trimethylchlorosilane (BSTFA+TMCS)		
Dichloromethane	LiChroSolv	Merck
Deuterated internal standards		
Cycolhexanecarboxylic acid		
C7 to C30 saturated alkanes mixture	Supelco, TraceCERT	Sigma Aldrich
2-(4-Hydroxyphenyl)ethanol		
Magnesium sulfate	ReagentPlus, Redi-Dri	Sigma Aldrich
2-Naphthoic acid		
Octanoic acid		
n-Hexane	SupraSolv for gas chromatography MS	Merck
Phenol		

 Table B.16: List chemicals and reagents used in the GCxGC sample preparation and analysis.

Thanks for reading.

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